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Compton profile of vanadium carbide and vanadium nitride

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A self-consistent, all-electron calculation was carried out for vanadium carbide and vanadium nitride using the linear-combination-of-Gaussian-orbitals method. Results are presented and discussed in light of existing theoretical and experimental data for partial density of states, total density of states, charge analysis, and Compton profile. From the comparison of the two compounds a pronounced change in the nonmetal *p* and vanadium *d* interaction is found, and is discussed in connection with the binding mechanism and directional anisotropies. [S0163-1829(96)09319-8]

I. INTRODUCTION

Transition-metal monocarbides and mononitrides, which have a simple rocksalt structure, continue to be studied by researchers because of their interesting physical and chemical properties. They have extreme hardness and high melting points, properties which are typical of covalent crystals, as well as metallic conductivities comparable to those of pure transition metals. These properties suggest that covalent, ionic, and metallic bondings are present simultaneously. Thus these compounds are not only valuable technological materials, but are also of special theoretical interest, in particular with regard to the electronic structure.

The purpose of this paper is to study in detail the electronic structure of vanadium carbide in comparison with vanadium nitride. Several calculations have been carried out on vanadium carbide and vanadium nitride, starting with the work of Bilz,[1] who used the tight-binding method. In many of these studies, vacancy effects have also been considered, as these compounds have a tendency to form nonstoichiometrically. In view of very useful reports[2–4] on various aspects of these compounds, here we shall refer to only a few reports which we consider important. Neckel *et al.*[5] carried out augmented-plane-wave calculations on these compounds with the linear-combination-of-atomic-orbitals (LCAO) interpolation scheme. The total and the partial density of states (DOS), along with a charge analysis, were presented. A subsequent report by Pai, Sathe, and Marathe,[6] utilizing charge self-consistent LCAO band-structure calculations on some transition-metal compounds, provides important information on these compounds. Further, a recent investigation by Bandyopadhyay, Saha, and Chatterjee[7] of isotropic Compton profile of vanadium carbide has been carried out using 59.54-keV gamma radiation. The experimental results were compared with the calculated Compton profile within the framework of renormalized free-atom (RFA) model.

The methods used to calculate the band structure employ a number of approximations and assumptions. The agreement with the experiment is often partial. This leaves a scope for more systematic work. In the present calculation a self-consistent linear-combination-of-Gaussian-orbitals (LCGO) method has been used to calculate the density of states from band-structure calculations. In addition, this calculation also gives the anisotropic Compton profile and a spherically averaged isotropic Compton profile of the two compounds. Our calculation differs from the previous calculation of Ref. 5 by the fact that we considered the metal 4*s* band, while in Ref. 5 the metal 4*s* band is omitted in the LCAO scheme.

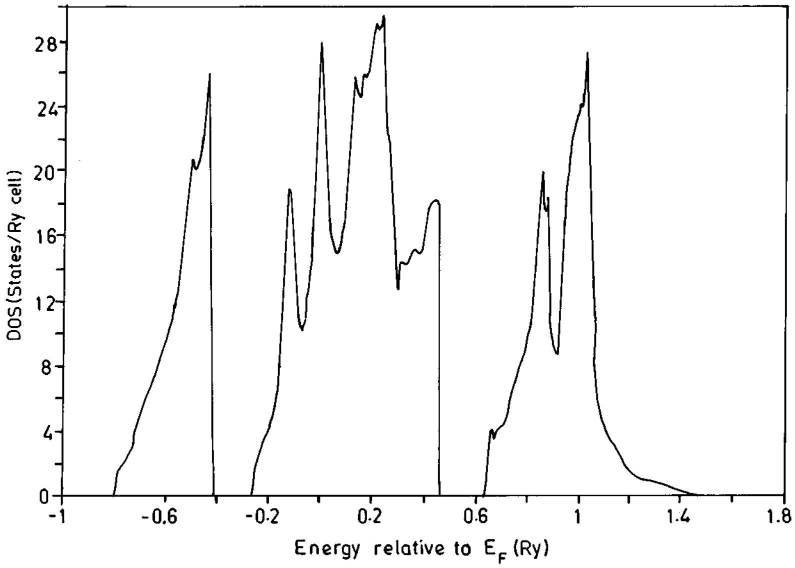

FIG. 1. Calculated total DOS of vanadium carbide.

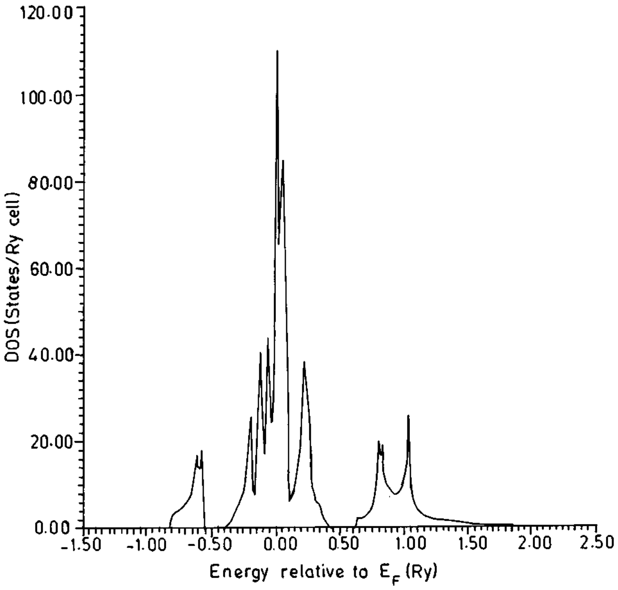

FIG. 2. Calculated total DOS of vanadium nitride.

Here we also present a comparison of the calculated results of vanadium carbide and vanadium nitride, which we consider to be significant for a determination of Gaussian wave functions, and which will lead to a better understanding of the electronic structure of these two compounds.

Our computational procedures are briefly described in Sec. II. The partial density of states and the total density of states under normal conditions are presented in Sec. III, while the charge analysis is presented in Sec. IV. Our results are compared with those of the previous calculations. Section V contains results for Compton profile, and finally our conclusions are summarized in Sec. VI.

II. COMPUTATIONAL METHOD

We have used the LCGO method. Calculations are made based on the local-density approximation to the density-functional theory. This method has been successfully applied to several metals.[8–12]

The Bloch wave functions needed in the self-consistent calculations were expanded in a set of independent Gaussian orbitals including in these cases 13 of s symmetry, ten p, five d, and one f in the case of vanadium, while for carbon and nitrogen we used nine of s-symmetry, six of p, and one of d, respectively. It may be noted that for vanadium an extra p orbital and an f orbital were added, and the most diffuse s orbital was deleted from the original table.[13,14]

The Coulomb and exchange-correlation potentials are expanded in a Fourier series. The Gaussian orbitals facilitates the analytic evaluation of the integrals which occur. A Ewald-type procedure has been evolved to facilitate convergence. Calculation of the Fourier coefficients of the exchange-correlation potential requires numerical integration. Here the unit cell is divided into a touching sphere, and $V_{\mathrm{xo}}(\mathbf{r})$ is expanded in Kubic harmonics and integrated by Filon's method. For integration over the interstitial region a least-squares fit is made to $V_{\mathrm{xo}}(\mathbf{r})$ in this region using only an auxiliary Fourier series. The series thus obtained, whose Fourier coefficients will be denoted by $V_{\mathrm{xo}}(\mathbf{k})$ is rapidly convergent, and is able to reproduce the potential in the interstitial region to 6–10 significant digits. A Fourier series is then defined which reproduces the same potential in the interstitial region, but is zero inside the muffin-tin sphere. The Hamiltonian and the overlap matrices considered in the computations are of dimension 75×75 for vanadium and 32×32 for carbon and nitrogen. The lattice constants in Å for vanadium carbide and vanadium nitride were taken to be 4.30 and 4.28, respectively. The compounds studied here have a rock-salt structure and a fcc bravais lattice. The basis consists of one type of atom at (0,0,0) and the other type at $(a/2)(1,0,0)$ of the conventional cubic cell.

In the calculations the iterations leading to self-consistency were carried out using 89 points for both vanadium and carbon in vanadium carbide, vanadium, and nitrogen in vanadium nitride, in $\frac{1}{48}$ of the Brillouin zone, and the linear tetrahedron integration scheme[15–18] until the change in the leading Fourier coefficient of the potential became 10^{-4} Ry or less. After establishing the self-consistency, the energy

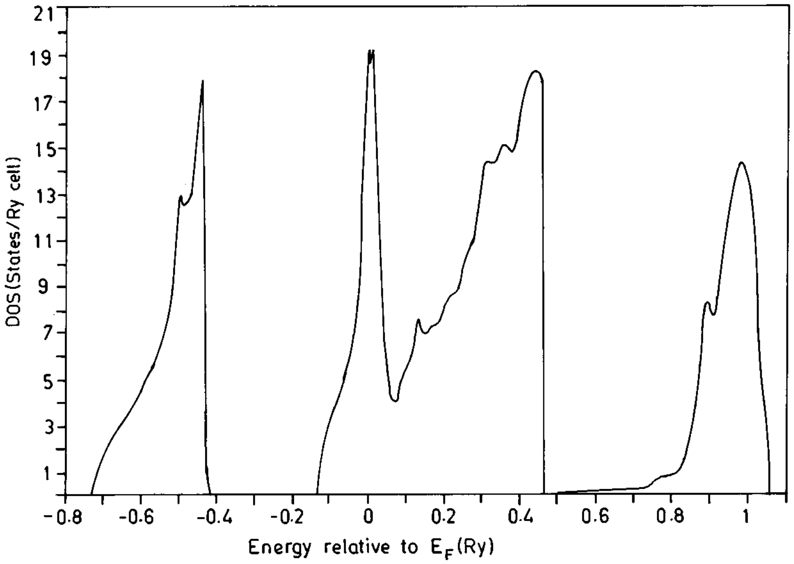

FIG. 3. Partial density of states (states of both spin per Ry and unit cell) of $3d$ and $4s$ orbitals of vanadium in vanadium carbide.

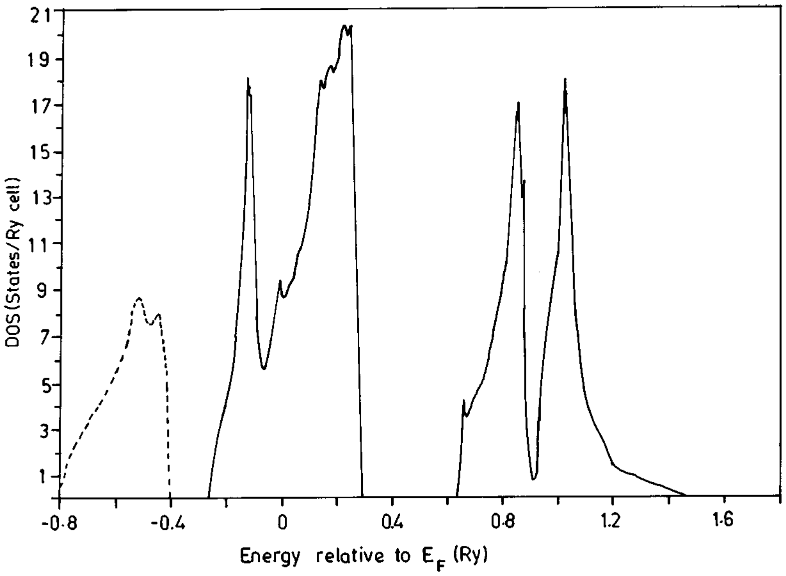

FIG. 4. Partial density of states (states of both spin per Ry and unit cell) of carbon in vanadium carbide. The broken and the full curves show the s-partial and p-partial DOS (states/Ry cell) of carbon. Broken curves: $g_s^C(E)$. Full curves: $g_p^C(E)$.

levels and wave functions were evaluated at the same number of points, and related properties were calculated with this grid.

III. DENSITY OF STATES

The DOS were calculated using the linear tetrahedron method,[15–18] using 89 points in an irreducible wedge of the Brillouin zone, and is shown in Fig. 1 for vanadium carbide and Fig. 2 for vanadium nitride. A systematic variation in the number of points did not show any appreciable improvement of the results with an increase in the number of **k** points.

The DOS is calculated using the equation

$$G(E)=\frac{\Omega}{(2\Pi)^3}\int d^3k\ \delta[E-E_n(k)], \tag{1}$$

where the integration is over the Brillouin zone. By using the nonmetal $2s$ and $2p$ and metal $3d$ and $4s$ Gaussian orbitals as basis functions, the density of states $G(E)$ can be decomposed into

$$G(E)=g_s^X(E)+g_p^X(E)+g_{d,s}^M(E), \tag{2}$$

where the superscripts X and M represent nonmetal and metal atoms, respectively. The decomposition of the densities of states into the partial densities of states are shown in Figs. 3 and 4 for vanadium carbide, and in Figs. 5 and 6 for vanadium nitride.

From the partial densities of states (Figs. 3–6), it can be seen that a nonmetal s band is separated by a gap from the higher valence bands. It is a characteristic feature of this class of compounds that the metal s states (V $4s$ in the present case) which are occupied in the atom and also in the bulk metal are raised above E_F in the solid compound. Figures 2, 5, and 6 show that for vanadium nitride the s band consists mainly of $g_s^{\mathrm{N}}(E)$. The p band has comparable contributions from $g_p^{\mathrm{N}}(E)$ and $g_{d,s}^{\mathrm{V}}(E)$. In the d band (up to about 0.2 Ry) $g_d^{\mathrm{V}}(E)$ dominates. In the energy range above 0.2 Ry the wave functions used are no longer strongly confined to the atomic spheres, but are more delocalized or free-electron-like. It is important to note here that with a rigid band-structure model (assuming constant partial densities of states) it is difficult to conclude why charge transfers are comparable for vanadium carbide and vanadium nitride. By using the results for vanadium carbide, the additional valence electron of nitrogen in vanadium nitride would primarily occupy d states, which are mainly localized inside the vanadium sphere. So, unless one takes into account the fact that the p band changes character, a drastic change in the charge transfer would result in the sequence carbide, nitride, oxide, as discussed in Ref. 5.

It is also evident from the partial densities of states that a strong mixing takes place between the nonmetal p and metal d states in both the compounds. These interactions may be

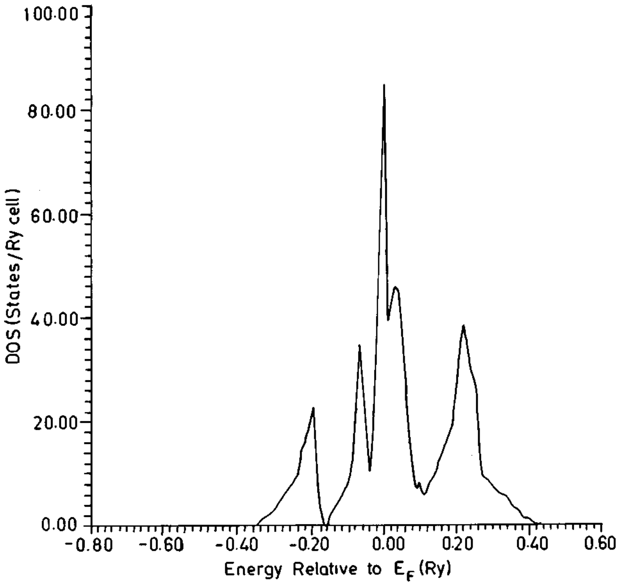

FIG. 5. Partial density of states (states of both spin per Ry and unit cell) of $3d$ and $4s$ orbitals of vanadium in vanadium nitride.

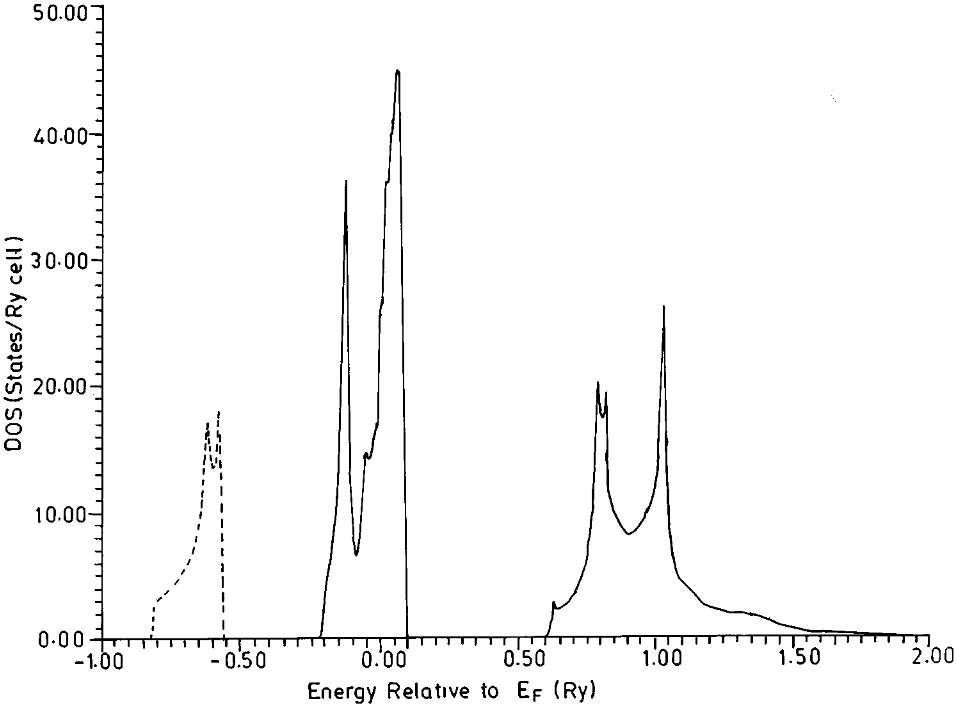

FIG. 6. Partial density of states (states of both spin per Ry and unit cell) of nitrogen in vanadium nitride. The broken and the full curves show the s-partial and p-partial DOS (states/Ry cell) of nitrogen. Broken curves: $g_s^{\mathrm{N}}(E)$. Full curves: $g_p^{\mathrm{N}}(E)$.

the cause of the high melting point and extreme hardness of these materials.

IV. CHARGE ANALYSIS

Integration of the partial densities of states, over all energies up to the Fermi energy, gives the partial charge which is given in Table I for vanadium carbide, and in Table II for vanadium nitride. The partial charges thus tabulated for vanadium carbide in this present work are in fairly good agreement with the results reported earlier by Neckel *et al.*,[5] while the charge analysis of Bandyopadhyay, Saha, and Chatterjee[7] shows a difference from the present calculation. This might be due to the approximation used in RFA calculations. Attention should be paid to the fact that here we have considered the $4s$ band for our calculation for both vanadium carbide and vanadium nitride, which was omitted by Neckel *et al.* in their LCAO scheme. This may have slightly altered the partial density of states of the d bands.

The valence bands of vanadium carbide and vanadium nitride originate mainly from the nonmetal $2s$ and $2p$ and vanadium-$3d$ states, as can be seen from Tables I and II as well as from the partial densities of states. It is also indicated that for vanadium carbide there is a charge transfer of about 1.8 electrons, while for vanadium nitride there is a charge transfer of about 1.4 electrons from the metal to the nonmetal sphere, which is slightly different from the values obtained by Neckel *et al.*[5] in their LCAO scheme. This anomaly in the results is presumably due to the choice of the orbital basis, where the former employed the Lowdin orbitals and we have chosen the Gaussian orbitals.

In the s band, which originates mainly from nonmetal $2s$ states, the s-like charge in the nonmetal sphere increases as we go from carbide to nitride as a consequence of the increasing localization of N $2s$ wave functions as compared with C $2s$. In the p band, where nonmetal $2p$ states make the main contribution, it is evident (from Tables I and II) that the nonmetal p charge C_p^X increases substantially going from carbide to nitride. Hence there is a clear change in the strong metal d nonmetal p hybridization between vanadium carbide and vanadium nitride. In the d band the charge from the additional valence electron in vanadium nitride primarily increases C_d^V.

TABLE I. Partial charges of vanadium carbide in units of number of electrons per unit cell. VEC: Valence-electron contribution.

	Neckel *et al.*	Bandyopadhyay, Saha, and Chatterjee	Present calculation
C_s^c	1.91		1.9836
C_p^c	3.66	4.80	3.8582
C_d^v and C_s^v			3.1582
C_d^v	3.43	2.20	
VEC	9.00		9.000

TABLE II. Partial charges of vanadium nitride in units of number electrons per unit cell. VEC: Valence-electron contribution.

	Neckel *et al.* (Ref. 5)	Present calculation
C_s^N	1.96	2.0068
C_p^N	4.20	4.3918
C_d^V and C_s^V		3.6014
C_d^V	3.84	
VEC	10.00	10.0000

TABLE III. Calculated Compton profile for vanadium carbide in the symmetry directions along with directional average.

q (a.u.)	$J_{[100]}$	$J_{[110]}$	$J_{[111]}$	$J_{\text{avg.}}$
0.0	8.412	8.639	8.583	8.550
0.1	8.092	8.292	8.246	8.233
0.2	8.012	8.145	8.124	8.100
0.3	7.899	7.950	7.961	7.938
0.4	7.710	7.689	7.729	7.700
0.5	7.223	7.155	7.213	7.190
0.6	6.560	6.477	6.536	6.510
0.7	6.009	5.935	5.979	5.960
0.8	5.514	5.465	5.487	5.480
0.9	5.175	5.158	5.158	5.160
1.0	4.474	4.486	4.473	4.470
1.1	4.076	4.106	4.090	4.090
1.2	3.718	3.754	3.741	3.740
1.3	3.412	3.441	3.433	3.431
1.4	3.158	3.171	3.169	3.160
1.5	2.841	2.835	2.840	2.838
1.6	2.551	2.532	2.541	2.540
1.7	2.514	2.488	2.501	2.499
1.8	2.279	2.254	2.267	2.265
1.9	2.078	2.059	2.068	2.066
2.0	1.905	1.892	1.893	1.900
2.1	1.707	1.700	1.702	1.703
2.2	1.582	1.579	1.578	1.580
2.3	1.516	1.516	1.514	1.515
2.4	1.429	1.430	1.427	1.429
2.5	1.350	1.351	1.347	1.349
2.6	1.274	1.275	1.270	1.273
2.7	1.203	1.203	1.199	1.202
2.8	1.147	1.147	1.143	1.146
2.9	1.089	1.088	1.083	1.087
3.0	1.037	1.034	1.030	1.035
3.5	0.865	0.855	0.852	0.857
4.0	0.735	0.721	0.714	0.723
4.5	0.639	0.621	0.618	0.626
5.0	0.541	0.531	0.530	0.530
5.5	0.470	0.475	0.470	0.473
6.0	0.380	0.373	0.380	0.380
7.0	0.279	0.281	0.281	0.280

TABLE IV. Calculated Compton profile for vanadium nitride in the symmetry directions along with directional average.

q (a.u.)	$J_{[100]}$	$J_{[110]}$	$J_{[111]}$	J_{avg}
0.0	8.856	8.918	8.890	8.896
0.1	8.818	8.858	8.835	8.841
0.2	8.699	8.702	8.694	8.699
0.3	8.504	8.463	8.474	8.478
0.4	8.228	8.151	8.177	8.180
0.5	7.864	7.772	7.801	7.806
0.6	7.416	7.332	7.350	7.361
0.7	6.934	6.877	6.874	6.893
0.8	6.414	6.396	6.370	6.395
0.9	5.899	5.917	5.877	5.903
1.0	5.412	5.459	5.415	5.434
1.1	4.924	4.982	4.946	4.956
1.2	4.563	4.619	4.597	4.597
1.3	4.163	4.208	4.200	4.193
1.4	3.862	3.890	3.897	3.884
1.5	3.533	3.546	3.565	3.547
1.6	3.268	3.269	3.298	3.276
1.7	2.999	2.994	3.032	3.004
1.8	2.758	2.751	2.786	2.762
1.9	2.542	2.535	2.564	2.545
2.0	2.351	2.348	2.367	2.353
2.1	2.185	2.186	2.194	2.188
2.2	2.033	2.041	2.038	2.038
2.3	1.895	1.909	1.898	1.902
2.4	1.767	1.786	1.772	1.777
2.5	1.658	1.679	1.665	1.669
2.6	1.558	1.576	1.566	1.568
2.7	1.468	1.479	1.475	1.475
2.8	1.368	1.389	1.390	1.388
2.9	1.309	1.305	1.310	1.307
3.0	1.239	1.230	1.238	1.235
3.5	0.983	0.986	0.984	0.985
4.0	0.798	0.795	0.796	0.796
4.5	0.666	0.665	0.665	0.665
5.0	0.560	0.561	0.560	0.560
5.5	0.477	0.476	0.477	0.476
6.0	0.405	0.406	0.405	0.406
7.0	0.293	0.293	0.293	0.293

V. COMPTON PROFILE

The Compton scattering technique to study electron momentum distributions has been a well-established method, and it has been used extensively during the last two decades. Experimental measurements with the use of energy dispersive detectors and high-energy gamma-ray sources have extended the application of this method to heavier solids like transition-metal compounds. An analysis of the Compton profile provides a critical test of the band wave functions, and provides important information on some features of the Fermi surface.

In our computational work we have only considered the valence-electron contribution to the Compton profile. This is due to the fact that Hartree-Fock contribution of core electrons for both compounds can be evaluated from the literature.[19] As the core electrons do not differ appreciably in the solid from those in case of a free atom, a free-atom core contribution for vanadium, carbon, and nitrogen would suffice to account for the total Compton profile of vanadium carbide and vanadium nitride.

The basic definition of Compton profile is given as

$$J_{\hat{k}}(q)=\frac{\Omega}{(2\pi)^3}\int d^3p\,\rho(\mathbf{p})\,\delta(q-\mathbf{p}\cdot\hat{\mathbf{k}}), \tag{3}$$

where $\rho(\mathbf{p})$ is the momentum distribution function, $\mathbf{k}$ is the change in momentum after a Compton scattering has occurred, $\hat{\mathbf{k}}=\mathbf{k}/|\mathbf{k}|$, Ω is the volume of the unit cell, and

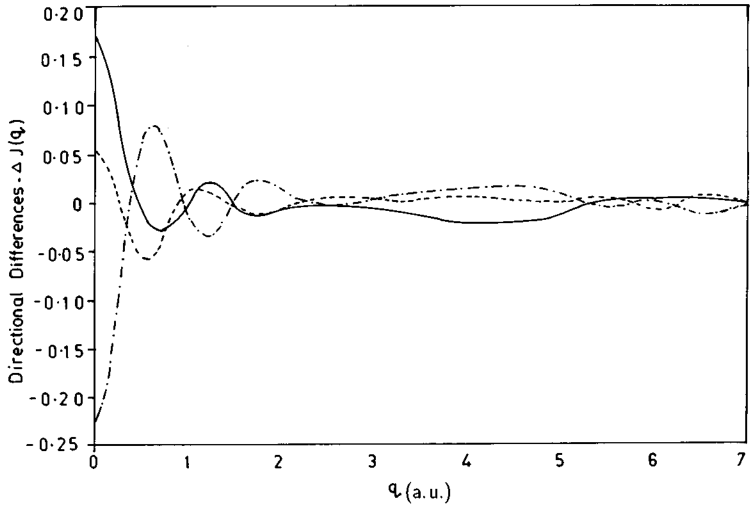

FIG. 7. Theoretical anisotropy curves of the Compton profile of vanadium carbide. The full curve represents the $J_{[111]}-J_{[100]}$ anisotropy, the dashed dot curve represents the $J_{[100]}-J_{[110]}$ anisotropy, and the broken curve represents the $J_{[110]}-J_{[111]}$ anisotropy, respectively. — represents $J_{[111]}-J_{[100]}$. -·-·-·- represents $J_{[100]}-J_{[110]}$. ----- represents $J_{[110]}-J_{[111]}$.

$$q=\frac{m\omega}{|\mathbf{k}|}-\tfrac{1}{2}(|\mathbf{k}|), \tag{4}$$

where $\hbar\omega$ is the energy transferred to the electron.

The Compton profiles $J_{\hat{k}}(q)$ for [100], [110], and [111] directions, and also the spherical average for some selected values of q ranging from 0 to 7 a.u., are given in the Tables III and IV for vanadium carbide and vanadium nitride, respectively. For comparison with the experimental values of vanadium carbide, the theoretical results were convoluted by using the resolution function and normalization factor of Bandyopadhyay, Saha, and Chatterjee.[7] The anisotropic Compton profiles are plotted in Figs. 7 and 8 for vanadium carbide and vanadium nitride, respectively, by calculating the differences of the Compton profiles with respect to directions of the momentum transfer. It is seen that for both compounds the high-momentum anisotropy is mainly due to [110], which suggests that any *d* bonding present will be along that direction. The fact that the [111]-[100] anisotropy is very small in the high-momentum region for both compounds is because both directions cut the [110] bond at roughly the same angle, and thus to first order the bond looks the same. At present, the experimental measurement of the isotropic Compton profile of vanadium carbide using 59.54-keV gamma radiation has been carried out by Bandyopadhyay, Saha, and Chatterjee.[7] We compare their results with our calculated values of the Compton profile in Fig. 9. We obtained our theoretical curve by adding to the calculated average of the Compton profile the necessary core contribution from Biggs, Mendelsohn, and Mann.[19] It is evident from Fig. 9 that our theoretical results compare well with the experimental findings. On the other hand, at present, there are apparently no experimental results for the Compton profile for vanadium nitride, hence only the theoretically calculated Compton profile is plotted in Fig. 10.

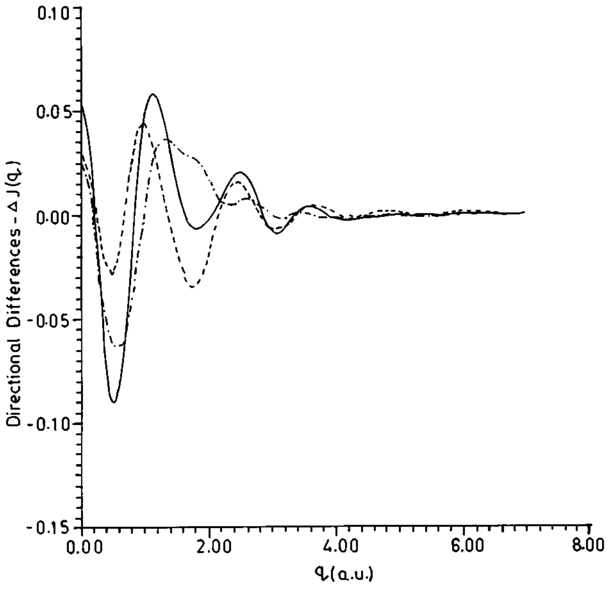

FIG. 8. Theoretical anisotropy curves of the Compton profile of vanadium nitride. The full curve represents the $J_{[110]}-J_{[100]}$ anisotropy, the dashed dot curve represents the $J_{[111]}-J_{[100]}$ anisotropy, and the broken curve represents the $J_{[110]}-J_{[111]}$ anisotropy, respectively. -·-·-·- represents $J_{[111]}-J_{[100]}$, — represents $J_{[110]}-J_{[100]}$, ----- represents $J_{[110]}-J_{[111]}$.

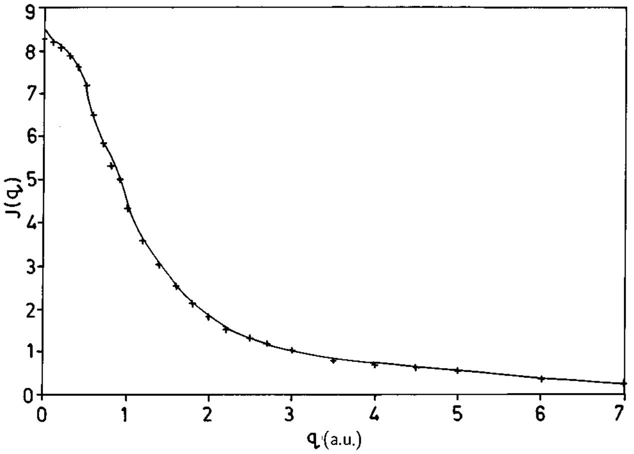

FIG. 9. Total Compton profile of vanadium carbide. The solid curve is from the present calculation, and the plus symbols represent the experimental points.

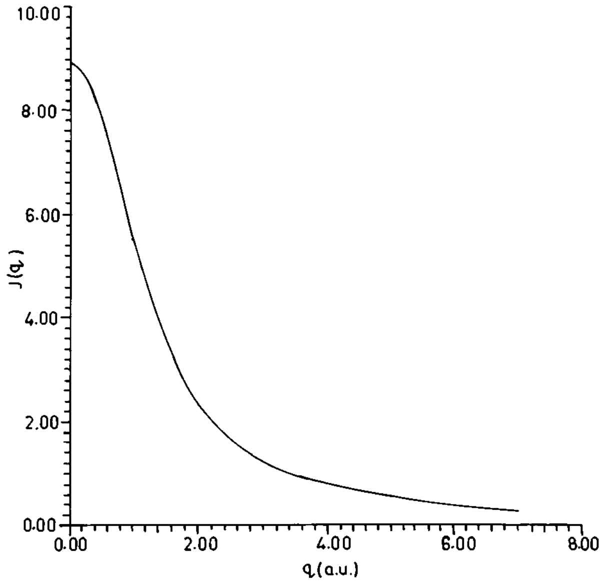

FIG. 10. Total Compton profile of vanadium nitride.

Since vanadium nitride and vanadium carbide both have the same rocksalt structure, roughly the same lattice constant, and a similar type of electrons participating in the bonding, it is not surprising that the anisotropies of the Compton profile are similar. It is interesting to note here that the reduction in the width of the occupied part of the $2p$ and $3d$ bands in the case of overlap, as pointed out by Neckel *et al.*,[5] in going from vanadium nitride to vanadium carbide is expected to explain the differences in our calculated low-momentum anisotropy (free-electron contribution).

VI. DISCUSSION AND CONCLUSION

We have presented a comparison of the experimental isotropic Compton profile of vanadium carbide with our theoretical results, and have included results on the Compton profile and directional anisotropies of vanadium nitride employing the LCGO method. The same model has been used for both compounds in order to establish a basis to search for trends in the binding properties. Since the two compounds are similar as regards their structure, we are justified in assuming that in a comparison of the two compounds the approximations involved would cancel to a large extent, yielding reliable results.

The importance of the metal d and the nonmetal p interaction is pointed in our work. A significant change in the binding character of the p band occurs between vanadium carbide and vanadium nitride. This has consequence for the charge transfer. From our charge analysis for vanadium carbide and vanadium nitride it is evident that neither the vanadium $3d$ nor nonmetal $2p$ shell is filled up. This unusual bonding nature may be the reason for the peculiar properties of these compounds. The density of states of vanadium carbide and vanadium nitride using the LCGO method have been calculated in the present work. There is a large enhancement of the density of states at the Fermi energy for these compounds, presumable[4] due to the electron-phonon interaction. Again it is observed that in the high-momentum region the anisotropy is large in the direction of the nearest neighbor, i.e., in the [110] direction. This suggest that the d bonding present would act along this direction for both vanadium carbide and vanadium nitride. To our knowledge this is the first report of the theoretical calculation of the Compton profile of vanadium carbide and vanadium nitride based on the LCGO method. The importance of this work lies in the fact that here we report the directional Compton profile and theoretical anisotropy of vanadium carbide and vanadium nitride.

Finally it is important to mention that the Compton profiles and the anisotropy are expected to provide a stringent test for the nonmetal p- and metal d-like wave functions in these systems.

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