Compton Profile of Boron Nitride *

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The Compton profile of hexagonal boron nitride has been measured using 59.54 keV gamma rays and a planar Ge detector. The results are compared with theoretical Compton profiles calculated for various ionic arrangements and with those available from a bond orbital model, LCAO and SC canonical HF calculations. The LCAO calculation is in relatively good agreement with the present measurement.

Key words: Compton profile; Electron momentum distribution; Hartree–Fock calculation; Ionic model; Linear combination of atomic orbitals.

I. Introduction

Boron nitride has remarkable properties and can be used to make a material as hard as diamond. It also behaves like an electric insulator but conducts heat like a metal [1]. It is isoelectronic to carbon and is known in cubic as well as hexagonal polymorphs, the most usual form being the hexagonal one (called h-BN). It is a highly anisotropic layered compound. The electronic structure in h-BN has been studied extensively by optical reflectivity and absorption, photoemission, X-ray emission, energy-loss and core-level spectroscopy by several workers [2]. Likewise, theoretical calculations employing various methods such as OPW, tight binding etc. have been made to determine its band structure and explain its various optical and other properties. Despite all this work, the situation is not satisfactory, as aptly summed by Robertson [2].

Within the last two decades, Compton scattering has emerged as a powerful tool for the investigation of the behaviour of valence electrons [3]. For polycrystalline h-BN, Compton profiles were measured in the early 70s using X-rays [4]. The data from these measurements are unlikely to have great physical significance owing to the well-known limitations of the earlier X-ray data (see, for example, [3]). In this paper we present γ-ray Compton profile data and compare them with the available theoretical results. We have also compared these results with theoretical Compton profiles for h-BN choosing several models of electron distribution between B and N atoms with a view to examine the effects of charge transfer on the Compton profiles in this system. The experimental details are given in the next section. The results and their discussion are presented in Section III.

II. Experiment

The samples were pellets prepared from high-purity (better than 99.9%) polycrystalline boron-nitride powder. The structure was confirmed to be hexagonal with $a = 2.51$ Å and $c = 6.67$ Å by powder diffraction. Two pellets of thickness 1.2 mm and 2.47 mm were prepared by pressing the powder in a steel die with a hydraulic pressure of about $7 \cdot 10^7$ N/m^2. Their densities were respectively 0.6 and 0.5 times the bulk value. Since the details of our Compton spectrometer have already been published [5], only a brief summary is given here. Gamma-rays from a 5 Ci annular ^{241}Am source were scattered by the sample through a mean scattering angle of 160° ($\pm 2.5°$) and detected using a planar intrinsic Ge detector. The channel width was about 58.6 eV, which corresponds to a little less than 0.1 p_0 ($p_0 = 1$ a.u. of momentum $= 1.99289 \cdot 10^{-24}$ kg m/s). About $4 \cdot 10^5$ and $8 \cdot 10^5$ counts/channel were collected at the Compton peak during the same exposure time of $1.5 \cdot 10^5$ sec for the thin and thick pellet, respectively. The Compton peak-to-background

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Table 1. Theoretical and experimental Compton profiles of polycrystalline BN. All the values are normalised to 5.91 electrons equal to the area under 0 to $+7\,p_0$. Theoretical values have been convoluted with the RIF. All profile data are given in multiples of p_0^{-1}.

p_z/p_0	$B^{+3}N^{-3}$	Bond-orbital model	LCAO	SHF	Exp.* [15]	Present experiment
0.0	4.211	4.911	4.233	4.172	4.151 ± 0.008	4.378 ± 0.012
0.1	4.200	4.849	4.213	4.155	4.128	4.361
0.2	4.163	4.716	4.157	4.101	4.064	4.294
0.3	4.072	4.476	4.061	4.011	3.958	4.179
0.4	3.913	4.186	3.929	3.888	3.814	4.018
0.5	3.760	3.834	3.762	3.732	3.638	3.812
0.6	3.392	3.465	3.561	3.545	3.422	3.566
0.7	3.076	3.084	3.330	3.326	3.176	3.286
0.8	2.762	2.719	3.069	3.078	2.908	2.984
0.9	2.469	2.379	2.787	2.804	–	2.668
1.0	2.195	2.074	2.487	2.511	2.345	2.353 ± 0.008
1.2	1.740	1.580	1.879	1.910	1.814	1.765
1.4	1.380	1.224	1.339	1.375	1.374	1.291
1.6	1.176	0.974	0.944	0.981	1.051	0.958
1.8	0.887	0.788	0.711	0.741	0.828	0.747
2.0	0.737	0.652	0.594	0.609	0.683 ± 0.004	0.615
2.5	0.504	0.451	0.447	0.446	–	0.432
3.0	0.357	0.339	0.334	0.335	0.361	0.328
3.5	0.259	0.254	0.255	0.256	–	0.256
4.0	0.195	0.194	0.196	0.196	0.221	0.197
5.0	0.114	0.108	0.118	0.111	0.139	0.119 ± 0.002
6.0	0.065	0.066	0.067	0.067	–	0.072
7.0	0.040	0.040	0.040	0.040	–	0.045

* Weighted average of $J_{\parallel}$ and $J_{\perp}$ values reported by Tyk et al. [15].

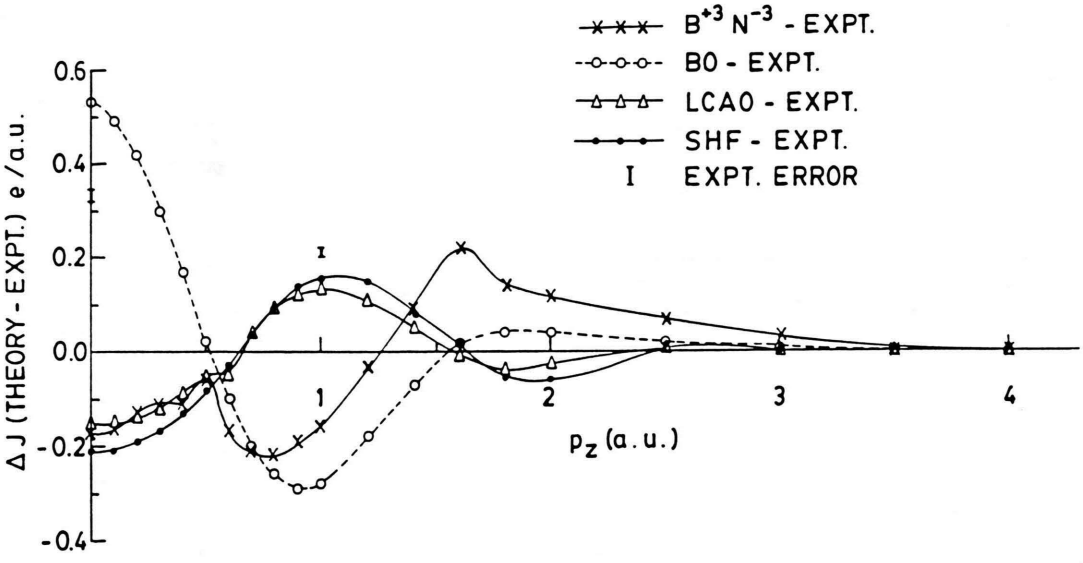

Fig. 1. Difference (ΔJ) profiles for polycrystalline h-BN. The theory has been convoluted with the residual instrumental function.

ratios were about 870:1 and 1650:1 for the thin and the thick sample, respectively.

After the subtraction of the background, the data were corrected for (i) instrumental resolution, (ii) sample absoprtion, (iii) energy dependence of the differential Compton cross-section and (iv) multiple scattering as per the procedure of Halonen et al. [6]. Finally the experimental Compton profiles corresponding to the high-energy side are normalised to have an area of 5.91, which is equal to the number of electrons in the free-atom profile in the region from 0 to $+7\,p_0$.

III. Results and Discussion

The experimental Compton profile for thin polycrystalline h-BN is presented in Table 1 (column 7). Also given here are the theoretical values from a ionic model, viz. $B^{+3}N^{-3}$, where the three valence electrons of the B atom are transferred to the 2p-orbitals of N. The Compton profiles for the core as well as the 2p-orbitals of the N atom were taken from the table of Weiss et al. [7]. We have also included in this table theoretical Compton profiles from other calculations based on the bond-orbital model of Lindner [8], an LCAO calculation of Dovesi et al. [9] and a self-consistent canonical Hartree-Fock calculation (SHF) of Euwema et al. [10]. It might be mentioned that in order to obtain valence LCAO and SHF Compton profiles, the spherical average of (100), (110) and (111) directional profiles of cubic BN [9, 10] was taken using the standard formula [5, 11]. The core contribution was added to obtain the total Compton profile. All theoretical values given in Table 1 are normalised to have an area of 5.91 electrons and are convoluted with the residual instrumental function (RIF) of our Compton spectrometer [5]. It is worthwhile to mention here that the spherically averaged Compton profile is almost independent of structure as mentioned by Ahuja et al. [12]. This is also supported by the work of Bacalis et al. [13] and Papanicolaou et al. [14], who have respectively assumed Ti and Zr to be fcc metals to calculate the isotropic Compton profile of these hcp metals. In column 6, the Compton profile obtained by a 1:2-weighted average of the $J_{\|}$ and $J_{\perp}$ values reported by Tyk et al. [15], which are similar, is given as an approximation to the true spherical average [16]. The comparison of the experimental Compton profile in column 6 (Tyk et al.) and our values in column 7 shows that up to 1.0 p_0 the values reported by Tyk et al. are lower than those of the present experiment, and after 0.8 p_0 the trend is reversed. But the overall agreement is good.

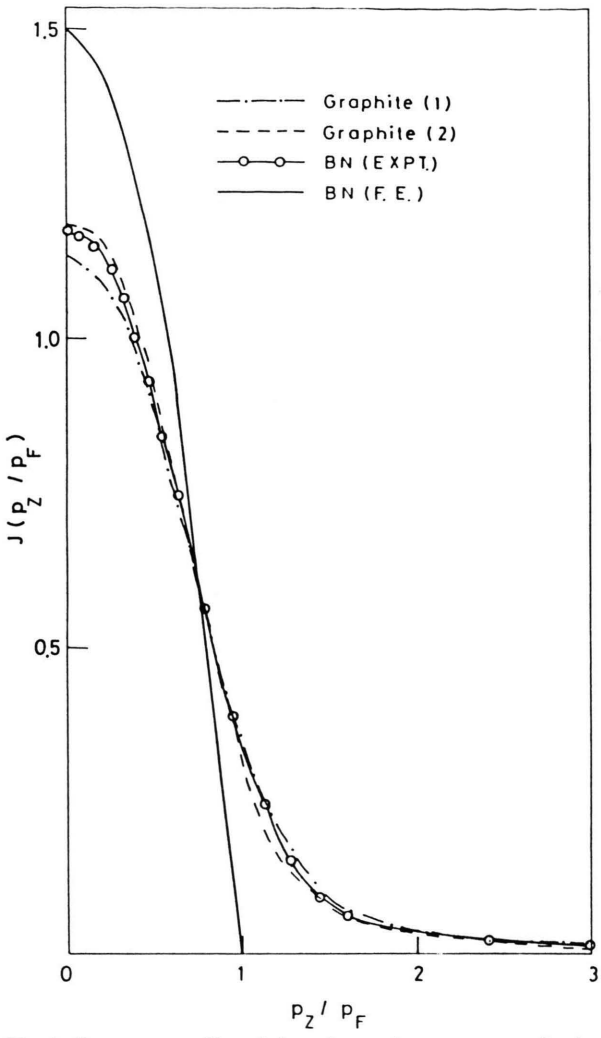

Fig. 2. Compton profiles of the valence electrons normalised to equal electron density for graphite and boron nitride. Experimental values for graphite (1) and graphite (2) are taken from [15] and [18], respectively. The solid line is the normalised Compton profile of a free electron gas containing eight electrons.

Next we compare the theoretical Compton profiles (columns 2–5) in the high-momentum region. Among ionic profiles, only $B^{+3}N^{-3}$ is taken for reasons discussed later on. It is to be noted that for $p_z > 3\,p_0$, a region dominated by core-electron contributions, all theoretical values are nearly equal and are close to the present experimental data. In order to compare the Compton profiles in the low-momentum region, we

plot in Fig. 1 the difference (ΔJ) between convoluted theory and experiment for different calculations. Error bars are also shown in this figure. Between $0-0.5\ p_0$, with the exception of the bond-orbital (BO) model, all theoretical values are lower than the experimental ones. The trend is reversed in the range $0.6-1.4\ p_0$ except for $B^{+3}N^{-3}$. After $1.4\ p_0$ all theoretical values except the ionic Compton profile are similar. Figure 1 clearly shows that the LCAO calculation represents the best agreement amongst these models, a fact confirmed also by the corresponding χ^2 values. Among ionic arrangements the value of χ^2 was the lowest for $B^{+3}N^{-3}$ and hence is given in the table.

However, even for the LCAO calculation [9] differences of about 3–5% remain in the low-momentum region. Some differences may arise from the samples having been prepared at high pressure because then the sample may contain preferential orientation of the crystallites and the data can deviate from the true spherical average owing to that effect.

Graphite and hexagonal boron nitride (h-BN) are isoelectronic compounds and have similar layered structures. The Compton profiles for graphite and h-BN appear to be different. In order to compare the actual behaviour of valence electrons and the Compton profiles of these compounds, we have plotted in Fig. 2 the equal-valence-electron-density experimental profiles (in units of p_z/p_F, where p_F is the Fermi momentum) as has been done earlier by Reed and Eisenberger [17] for diamond, Si and Ge. In the case of graphite, we have considered two earlier measurements [15, 18]. The data of Tyk et al. [15] are used by taking the average of $J_{\|}$ and $J_{\perp}$ as mentioned earlier. In the other data, Reed et al. [18] have underestimated the multiple-scattering correction. For this reason, we think that these data can only be used for a qualitative comparison. As expected, such a scaling gave us identical profiles for BN and graphite (as can be seen in Fig. 2) and thus clearly reveals identical bonding in these isoelectronic lubricant compounds.

It is also obvious that on the basis of the ionic model nearly 3 electrons are to be transferred from B to N, which is a very large value in disagreement with other estimates of the charge transfer, viz. 1.6 e by Kuzuba et al. [19]; 1.15 e by Green et al. [20] and 0.50 e by Dovesi et al. [9]. It is not difficult to understand the failure of the ionic model, because in our approach we have completely ignored the different spatial behaviour of electrons in σ- and π-bands.

IV. Conclusion

In this work it has been shown that for h-BN the LCAO model, despite the differences in the low-momentum region, agrees best with our experimental Compton profile. The amount of transferred charge comes to be about 3 e if only an ionic mechanism of bonding is considered. However, this conclusion is expected to be unreasonable in view of the fact that the σ-electrons, which are responsible for the strong bonding, would probably have a different momentum distribution than the π-electrons, a fact which has been neglected here. It would be possible to extract the distribution of electrons in these bands if we knew theoretically the electron momentum distributions for the s, σ and π-bands individually. It is also concluded that graphite and h-BN have the same bonding.

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