PHYSICAL REVIEW B VOLUME 15, NUMBER 4 15 FEBRUARY 1977

X-ray photoemission study of core-electron relaxation energies and valence-band formation of the linear alkanes. II. Solid-phase measurements

J. J. Pireaux* and R. Caudano

Facultés Universitaires N.D. de la Paix, Laboratoire de Spectroscopie Electronique, rue de Bruxelles, 61, B-5000 Namur, Belgium

(Received 20 September 1976)

Core and valence electronic levels of normal alkanes have been studied in the solid phase by means of x-ray photoelectron spectroscopy. By comparing the calibrated C 1*s* core-level binding energies with previous measurements in the gas phase, one estimates the magnitude of the polarization or the extra-molecular relaxation energy to be about 1.5 eV. The observed structures in the valence band from *n*-pentane to polyethylene are discussed in terms of the evolution of an electronic level to a band structure in a quasi-one-dimensional solid. Intermolecular interactions and crystal-field effect on solid-state electron energy distribution are studied by comparing gas- and solid-phase spectra. Long-range interatomic interactions in a tridimensional solid are analyzed through the comparison of the valence-band structures in polyethylene, graphite, and diamond.

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) allows the study of the energy levels occupied by electrons in atoms and molecules in gas, liquid, or solid phases.[1] When these atoms are periodically arranged in a crystal, their electrons are distributed within energy bands, characteristic of the solid. In this work, we propose to follow and analyze the construction mechanism of an electronic energy band from a discrete electronic level, during the progressive formation of a solid. Indeed the spectrum of a free atom is gradually modified as atoms are assembled to form a solid.

Let us take the following simple model. When two identical atoms are brought near each other to form a molecule, their electronic clouds overlap. As a result, the electronic levels doubly degenerated in this system split during the formation of the molecule. The energy splitting for an electronic level will be more pronounced for the outermost shells of the molecule where the overlap between the atomic orbitals is larger. Outer orbitals, which have larger radii and are loosely bound to their own nuclei, will be more affected by the perturbation. The Pauli exclusion rule then acts as the *aufbau* principle, i.e., it governs the distribution of the electrons on each molecular level. The considerations may be generalized to a polyatomic molecule containing an arbitrary number of identical atoms or groups of atoms. As the number of atoms in the molecules increases, the electronic level density will increase correspondingly, and gradually this will become a band structure.

An illustration of such a band-structure formation was recently reported in the XPS analysis of the 4*d* electronic band of small silver particles with varying size.[2] Indeed, at high coverages, i.e., for a larger size of the clusters, band structures characteristic of the solid are observed.

We found[3,4] that the alkanes series (formula $C_n H_{2n+2}, 1 \leqslant n < \infty$) is suitable to study step by step the formation of a band structure, the successive molecules with increasing number *n* being in fact considered as progressive steps in constructing a quasi-one-dimensional solid. As a first approach, it was chosen to work with gases, thereby avoiding the disturbing influence of intermolecular interactions. In a previous paper,[3] we have presented the x-ray photoemission spectra of the *n*-alkanes in the gas phase together with some *ab initio* molecular-orbital calculations.

In the present paper, we extend this study to the solid phase. Some alkane molecules previously studied[3] ($n = 5, 9, 13$) are reconsidered in the condensed phase, together with a few new compounds (alkanes with $n = 6, 7, 8, 10, 17, 26$).

Our work will be presented as follows. The experimental procedures are given in Sec. II. The corresponding core-level results are gathered in Sec. III, whereas valence-band spectra will then be discussed in Sec. IV.

II. EXPERIMENTAL

The normal alkanes were obtained commercially and used without further purification. Unless otherwise mentioned, they were at least of 99+% purity, and purchased from Aldrich chemicals [$n = 5, 6, 8, 10, 13, 17$ (99%), 36 (98%)], Merck ($n = 7, 9$), and Eastman-Kodak Co. ($n = 26$). In STP conditions, these molecules are in the liquid phase for $5 \leqslant n \leqslant 17$, and in the solid one for $n \geqslant 26$.

In order to be studied as solids in ultrahigh vacuum, most of these alkanes must be condensed on a cooled substrate. Therefore a special gas inlet system was adapted to the sample preparation chamber of the Hewlett-Packard 5950A ESCA Spectrometer. During the condensation process the gases were admitted *in situ* at a pressure of 10^{-5}–10^{-4} Torr and the residual gas pressure was estimated to be in the 10^{-8}-Torr region. After this procedure the vacuum recovered rapidly the 10^{-8} Torr in the preparation chamber and the analysis was performed at $(1-3)\times 10^{-9}$ Torr in the main chamber. The samples were irradiated with monochromatized Al $K\alpha$ radiations (1486.6 eV) and the photoejected electrons analyzed in energy in the conventional way.[5]

The alkanes are organic insulators and consequently the photoemission charges electrostatically these samples. The use of thin films, a few hundreds Å thick, reduces the importance of this effect. Charge neutralization can also be minimized by flooding low-energy electrons on the sample surface. We note that in these operating conditions, the charging shifts the measured binding energies by a constant amount but it does not significantly broaden the recorded structures.

It is rather difficult to calibrate the binding energy scale for these compounds. For instance any evaporation onto the sample surface, and gold especially, destroyed completely the volatil condensed alkane films. Mixing the alkane with another reference substance was not possible. We have therefore evaporated a very thin alkane film onto a gold substrate. In this case, we may suppose that a good electrical contact exists between the two layers, and calibrate the alkane C 1*s* signal relatively to the underlying Au $4f_{7/2}$ line, taken at 83.8 eV.[6]

III. CORE LEVELS

The experimental alkane ($n=5$ to 26) C 1*s* binding energies, relative to the Fermi level of the spectrometer, were measured to be all around the mean value of 284.6 eV with a deviation of 0.1 eV (90% confidence level).[4] These measurements are consistent with the binding energy of 284.6 eV calibrated for *n*-hexatricontane and polyethylene by the gold-decoration technique.[7] No significant chemical shift can then be assigned to the alkanes of increasing length in the solid phase. This situation contrasts with the gas-phase results where a very smooth variation of binding energies versus the number of C atoms in the molecules was recorded.[3,4]

The binding energy of an electron on a given level is always lower in the solid phase than in the gas phase. We measured this difference to be as much as 5.7 eV for the alkanes studied in both phases, i.e., molecules with $n=5,6,8,10$, and 13. This effect can be explained by two additive contributions: an extramolecular relaxation or polarization of the solid, and the difference between the reference levels used for the binding energies in each type of measurements.

Indeed, the ejection of an electron from a core level occurs simultaneously with a charge redistribution in the molecule: in the solid phase this reorganization is not limited to the neighboring atoms in this molecule,[3] but extends to a larger elementary volume in the solid. This new contribution, lowering the electron binding energy, corresponds to a polarization of the neighboring molecules in the solid.[8] This dielectric polarization energy of the solid can be evaluated within the hypothesis of a continuous matter and of a polarization simultaneous to the photoelectron emission. Then, if a spherical hole has an identical charge distribution to that of the free ion, the energy difference between this hole, screened by the solid medium and the free ion is

$$P=(e^2/4\pi\epsilon_0)\,(1-1/\epsilon)\,(1/r)\,,$$

with ϵ the dielectric constant of the solid, and r the averaged distance between the nearest neighbors.

Values for this energy P has been calculated for some alkanes to be close to 1.5 eV.[9] As the dielectric constant[10] and atomic interdistance, r are practically identical for all the alkanes we can suppose with a good accuracy that this energy of 1.5 eV is valid for all the studied molecules.

A comparison of the alkanes core binding energy in the gas (reference energy equal to vacuum level) and solid (reference energy equal to Fermi level) phases furthermore requires an evaluation of the work function Φ of the solid. Indeed,

$$E_{\text{vacuum}}=E_{\text{Fermi}}+\Phi\,.$$

The work function of polyethylene (the alkane of infinite chain) has been measured to be between 4.5 and 4.7 eV.[7,11] On the other hand, uv absorption measurements have shown that Φ is >4.2 eV for pentane and hexane.[9] Then taking 4.5 eV as a mean value of Φ for the alkanes, we obtain that relation

$$E_{\text{solid}}=E_{\text{gas}}-P-\Phi$$

is verified to within 0.3 eV.

IV. VALENCE LEVELS

A. Alkane molecular orbitals

The alkane molecular orbitals (MO) are simple, being composed of C 2*s*, C 2*p*, and H 1*s* atomic functions. The corresponding valence electrons are located within two energy bands of C 2*s* and

TABLE I. Experimental solid phase [(a) binding energy calibrated against the C 1*s* core level at 284.6 eV; the spectrometer Fermi level is used as an absolute reference] and theoretical [(b) *ab initio* (minimal basis) binding energies, calculated from the vacuum level of the molecule] binding energies of the alkanes electronic levels in the C 2*s* band. Units in eV.

	n-pentane		*n*-hexane		*n*-heptane		*n*-octane		*n*-nonane	
Peak	a	b	a	b	a	b	a	b	a	b
1	19.5	28.22	20.0	28.40	19.1	28.50	19.4	28.57		18.62
2	18.2	26.35	19.3	26.99		27.41		27.71	19.6	27.92
3	16.6	23.63	18.0	24.82	17.9	25.69	17.5	26.31		26.77
4	14.2	20.89	15.8	22.26	16.3	23.51		24.49	18.1	25.24
5		20.19	14.4	20.30	14.7	21.28	15.8	22.43	16.8	23.44
6				20.18	13.7	20.20		20.64	15.2	21.58
7						20.07	14.0	20.21		20.34
8								20.00	14.2	20.15
9										20.00

C 2*p* dominant character, respectively. These bands are separated by a large energy gap.[3,12] We shall orientate our analysis onto the MO of dominant C 2*s* character.

The XPS spectra from methane to *n*-tridecane ($n = 1$ to 13) in the gas phase have already been analyzed.[3] The valence-electron spectra of the alkanes with $n \geq 5$ recorded in the solid phase are shown in Figs. 1–6, and will be discussed individually. The valence lines are numbered from the left to the right in the spectra. Their binding energies are given in Table I with an estimated uncertainty of 0.2 eV.

The lighter alkanes ($n = 5, 6, 7$) were studied at low temperature in the range of 110–150 °K. In these conditions, after long runs of data accumulation over the valence-band region, an extra structure appears at a binding energy of about 26 eV. This peak originates from the O 2*s* level of water, which condenses onto the sample surface, from the residual gases in the analysis chamber. Fortunately, this structure does not interfere with those of the alkane molecular orbitals.

In order to interpret the experimental results in terms of MO energy levels, *ab initio* calculations were performed using a minimal basis set. These theoretical values are given in the second part of Table I. They also served to simulate the shape of the alkane C 2*s* band in the insets of Figs. 1–4. Therefore, δ functions located at the *ab initio* MO binding energies have been convoluted with a Gaussian function. An equal intensity weight was given to each component, neglecting the photoionization cross-section variation through the different MO. These synthesized spectra will be used to test the overall consistency of the assignments.

1. n-Pentane (Fig. 1)

In the C 2*s* band, the molecular-orbital energy levels of *n*-pentane appear as three intense structures. These peaks can be correlated to the five *ab initio* MO binding energies (inset Fig. 1 and Table I). The (sharper) central peak is the photoelectron image of a single MO, whereas each of the extreme ones corresponds to the sum of two MO. The two components (labeled 1 and 2) of the leftmost structure have been resolved by a graphical method[13] using Gaussian profiles and the full width at half-maximum of the central peak (No. 3) as a standard. The corresponding deduced energy gap between these maxima is 1.31 ± 0.05 eV (Table I). The correlation obtained between the experimental and theoretical binding energies is then satisfactory, as it is given by a straight line with a correlation coefficient $r^2 = 0.992$.

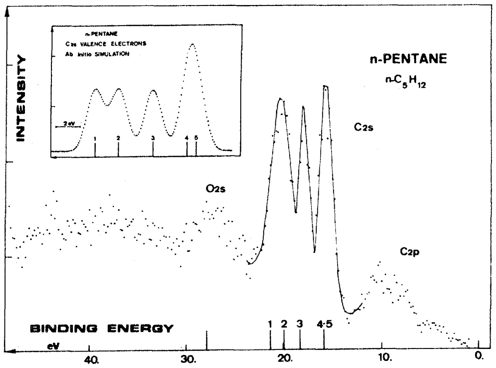

FIG. 1. Valence-electron spectrum of *n*-pentane. The inset shows a simulation of the C 2s band using *ab initio* calculations. Theoretical and experimental binding energies of the alkane molecular orbitals are reported in Table I.

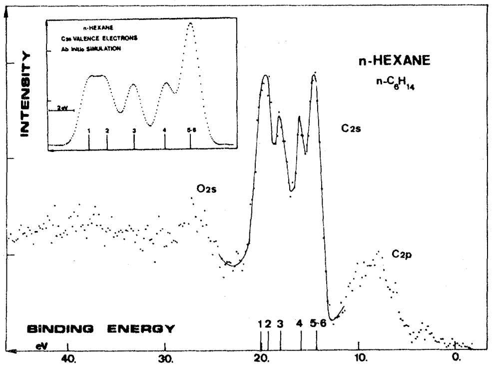

FIG. 2. Valence-electron spectrum of n-hexane. The inset shows a simulation of the C 2s band using *ab initio* calculations. Theoretical and experimental binding energies of the alkane molecular orbitals are reported in Table I.

2. *n-Hexane (Fig. 2)*

According to the *ab initio* calculations (Table I) the C 2s electrons of n-hexane are distributed between six MO. The convolution of this theoretical spectrum shows four major structures (inset Fig. 2) which are clearly resolved on the XPS spectrum (Fig. 2). The leftmost peak has been deconvoluted by the method mentioned above and gives a energy gap of 0.7 eV between the components 1 and 2. Again, by comparing these experimental and theoretical results, one finds that the linear correlation between the calculated and measured MO binding energies (Table I) is good ($r^2 = 0.995$).

3. *n-Heptane (Fig. 3)*

The C 2s valence electrons of n-heptane are distributed between seven MO. In the spectrum of Fig. 3, however, only three structures can be resolved. Still, comparing this measurement with the spectrum synthesized from the *ab initio* data (inset of Fig. 3), one concludes that three, one and three energy levels are contained, respectively, in each successive experimental peak. The second derivative of the spectrum has been calculated (lower curve in Fig. 3) to measure accurately these peak energies and to point out the fine structures.[14] In that manner, the binding energies obtained for the n-heptane MO are reported in Table I. Once more, the linear correlation with the theoretical binding energies is satisfactory ($r^2 = 0.987$).

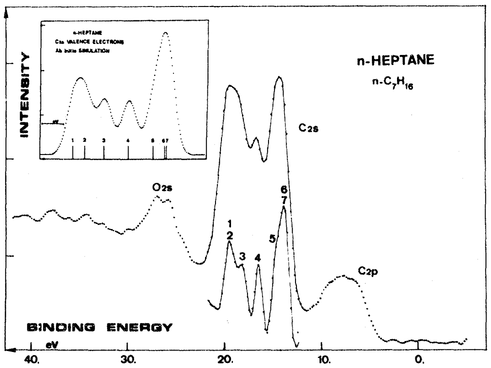

FIG. 3. Valence-electron spectrum of n-heptane. The inset shows a simulation of the C 2s band using *ab initio* calculations. Theoretical and experimental binding energies of the alkane molecular orbitals are reported in Table I.

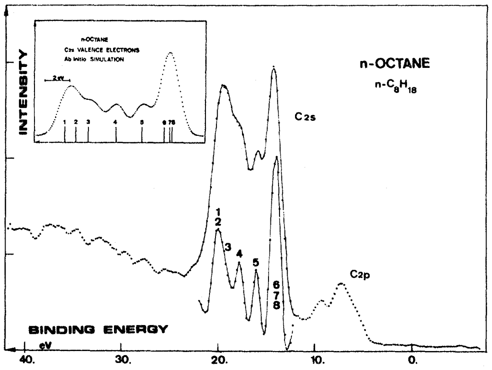

FIG. 4. Valence-electron spectrum of n-octane. The inset shows a simulation of the C 2s band using *ab initio* calculations. Theoretical and experimental (measured on the second derivative of the spectrum as shown on the lower curve) binding energies of the alkane molecular orbitals are reported in Table I.

4. *n-Octane (Fig. 4)*

In the C 2s valence region of n-octane only four distinct structures are found, whereas theoretical calculations predict eight MO in this band. The second derivative of the spectrum determines precisely the energies of the four observed peaks, which correlate reasonably with the *ab initio* values of Table I ($r^2 = 0.969$).

5. *n-Nonane (Fig. 5)*

Increasing further the size of the alkane chain results in spectra where the C 2s MO energy levels become progressively less and less resolved. Only few structures can be seen in the C 2s region of n-nonane, where nine orbitals are theoretically located. These peaks are more easily identified on the high-resolution recording and its corresponding 2d derivative presented in the inset of Fig. 5. The correlation coefficient obtained by comparing the experimental and theoretical binding energies is $r^2 = 0.978$, which sup-

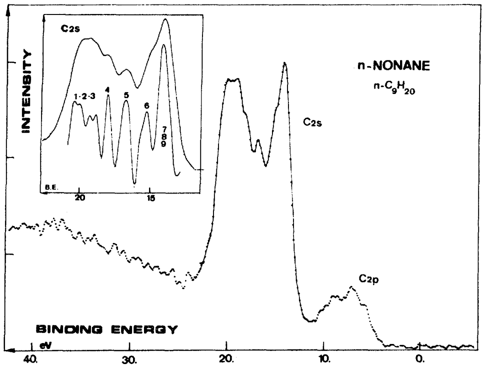

FIG. 5. Valence-electron spectrum of n-nonane. The inset shows a high-resolution spectrum of the C 2s band and its second derivative. Theoretical and experimental binding energies of the alkane molecular orbitals are reported in Table I.

ports favorably our MO assignment of the observed structures.

6. *n-Decane, n-tridecane, n-heptadecane, n-hexacosane, and n-hexatriacontane (Fig. 6)*

For longer molecules the electronic levels become more numerous in the C 2*s* band, and the experimental resolution does not allow one to resolve them any further. The XPS spectra of the alkanes with $n = 10, 13, 17, 26, 36$ look very similar to each other as one can see on Fig. 6. The C 2*s* band contains two peaks: a quite sharp one on the right, and a broader and more asymmetric one on the left. The energy gap between these two structures varies smoothly from 5.4 eV for $n = 10$, to 5.6 eV for $n = 36$; the C 2*s* bandwidth increases also slightly from 7.5 to 7.6 eV.

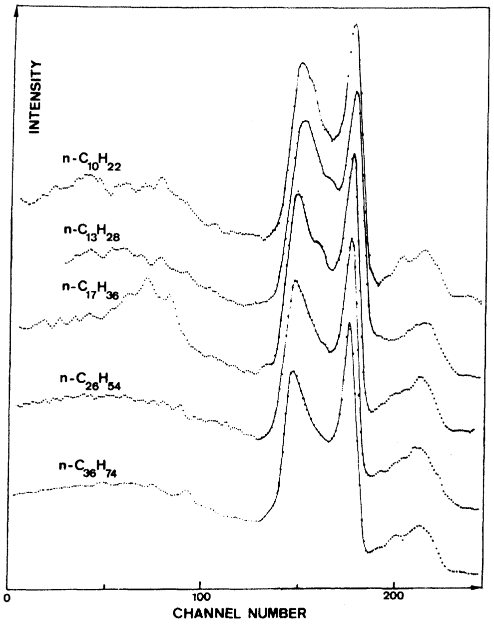

FIG. 6. Valence-electron spectra of n-decane, n-tridecane, n-heptadecane, n-hexacosane, and n-hexatriacontane.

7. *Polyethylene*

The XPS study of the valence-band structures of polyethylene (the alkane with practically infinite chain) has already been published.[7,15]

B. Formation of a band structure

The number of electronic levels in the alkane C 2*s* region is equal to the number of carbon atoms in the molecule chain. Since the C 2*s* band extends over a limited energy range of about 7.6 eV, the spacing between the individual energy levels decreases with increasing number of C atoms. Progressively, it becomes impossible to distinguish the isolated levels and, for larger n, the peaks overlap and form a band structure. By this process, the alkanes can be considered as progressive steps in the formation of a quasilinear one-dimensional infinite solid, polyethylene.

Considering Figs. 1–6, it is possible to evaluate the smallest number n, from which the ESCA (electron spectroscopy for chemical analysis) spectrum of any alkane will become essentially similar to the one of polyethylene. This gives the minimal system length necessary to successfully simulate the real band structure of an infinite solid. Figure 6 shows that for the alkanes almost all the fine structures disappeared in the C 2*s* band when $n > 10$. Moreover, the displayed spectra are quite similar to each other, and consequently to the spectrum of polyethylene.[7,15] Therefore we conclude that a dozen carbon atoms in the alkane chain is sufficient to simulate the electronic properties of polyethylene.[3,4]

This conclusion cannot be compared quantitatively to the results of Mason[2] who studied silver particles. In this case the sample preparation yields a statistical distribution of particle sizes, thus preventing any precise specification of the number of silver atoms in each cluster. Still, it seems that for a coverage of 5×10^{15} atoms/cm^2 the density of states of metallic silver particles is almost similar to the silver bulk metal. This would correspond to silver grains containing an average of an half-dozen atoms.

Recently, Messmer *et al.*[16] presented self-consistent-field $X\alpha$ calculations on the MO of metallic (Cu, Ni, Pd, Pt) clusters with increasing size. Their results suggest strongly that much of the bulk valence-band width and the principal

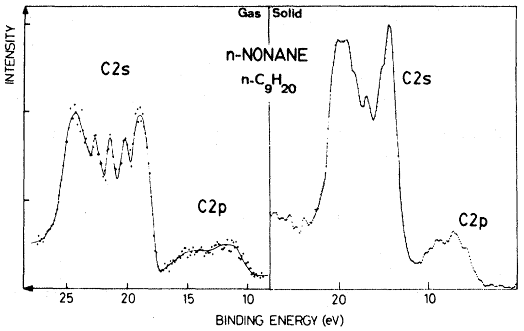

FIG. 7. Valence-electron spectra of n-nonane, recorded in the gas and solid phases.

features of the density-of-state structures can already be obtained with the short-range order of a particle containing approximately a dozen atoms. Let us point out also the extended study on the electronic structure of selenium aggregates by Hoareau *et al.*[17] which leads essentially to the same conclusion.

Valence-band spectra of some alkanes (n $=5, 9, 13$) have been recorded in both the gas and solid phases. These results can be used to evaluate the magnitude of the intermolecular interactions and crystal-field effect in the solid phase, which will modify the photoelectron energy distribution from the isolated molecules. Taking n-nonane as an example shows (Fig. 7) that the spectra are essentially similar in the two phases, presenting the same two structures in the C 2s band. Besides the inelastic background contribution, characteristic of the solid phase, and the arbitrary shift of the binding energy scale, the most significant difference between the two spectra is a slight increase of the peak widths recorded in the solid phase, although both spectrometers used for this study have practically the same line resolution. The only detectable phase-transition effect for the alkanes is thus a broadening of the lines.[1a] If we remember that the alkane molecules do not contain any polar group or dipole moment, it is easy to understand that the intermolecular interactions do not affect the solid-state spectra significantly.

Finally, it is interesting to extend part of our conclusions to a classical solid with a three-dimensional lattice. For this purpose we compare in Fig. 8 the valence-band structures of one-, two-, and three-dimensional arrays of carbon atoms, i.e., polyethylene,[7] graphite, and diamond,[18] respectively. These three spectra present essentially the same features: (i) a large peak (I) between 17 and 19 eV, (ii) a sharper structure (II) with different relative intensities on the spectra at 13–14 eV, and (iii) a wide and less intense band, below 10 eV of binding energy. As differences between these recordings one notices that peak I becomes dominating when going from polyethylene to diamond and to graphite whereas the intensity of peak II is strongly reduced; simultaneously, peak III becomes more diffuse and wider. The study of the electronic structure of the polyethylene valence band[7] has shown that structures I and II constitute a band with dominant C 2s atomic character, whereas structure III corresponds to a band with C 2p atomic symmetry. A theoretical analysis of the influence of photoionization cross section on the polyethylene electron-energy-distribution curve indicates a more pronounced C 2s character in peak I than in peak II.[19] The comparison of the XPS and x-ray emission spectra of diamond[18] leads to a similar conclusion, i.e., that peak II contains an appreciable mixing of s and p symmetries. The same distribution of electron

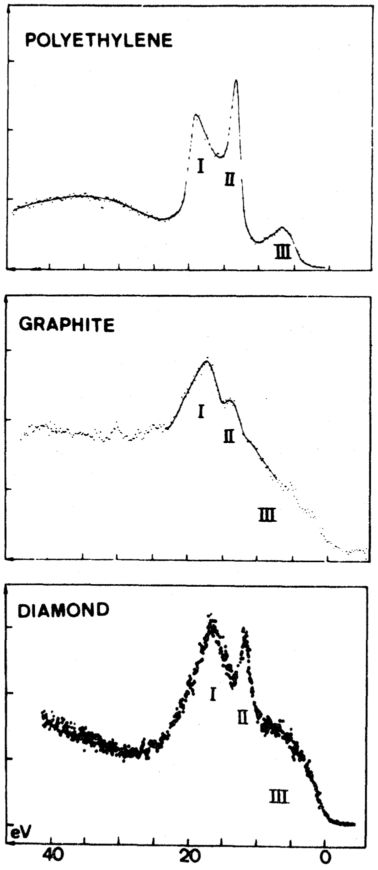

FIG. 8. Valence-electron spectra of polyethylene, graphite, and diamond (from Ref. 18), respectively, one-, two-, and three-dimensional arrays of carbon atoms.

symmetry has been calculated and measured within the graphite valence band.[18] But in this crystalline form, the poorer C 2*s* contribution in structure II explains that peak I appears wider and more intense on the spectrum. Indeed, the valence band of graphite contains a stronger 2*s* admixture (sp^2) relatively to diamond and polyethylene where C atoms are tetrahedrally bonded. This explains why the graphite spectrum is more differentiated than the two others. The slighter differences subsisting between diamond and polyethylene are due to the fact that, although they both have a tetrahedral coordination, in the former case each carbon has four identical neighbors and in the latter case two carbon and two hydrogen atoms. The overall resemblance between the recordings of Fig. 8 proves that the modifications in the electronic density of states are not so drastic when passing from a quasilinear solid to a three-dimensional crystal. We conclude therefore that the dominant characteristic of a density of states depends mainly on the atomic properties and on the short-range order in the crystal, whereas long-range order will account for the fine structures.

V. CONCLUSIONS

The comparison of the C 1*s* binding energies with the gas-phase data results in the estimation of 1.5 eV for the solid dielectric polarization or extramolecular relaxation energy.

Molecular-orbital energies from *ab initio* (minimal basis) calculations correlate successfully with the experimental valence-electron binding energies, supporting our discussion on the C 2*s* valence structures. The alkanes with increasing chain length have been considered as successive steps in the formation from an energy level to a valence band during the construction of an infinite quasilinear crystal, polyethylene. The C 2*s* region in the spectrum has nicely illustrated this evolution. As a consequence we have shown that a molecule containing a dozen carbon atoms presents a density of states essentially similar to the one of the infinite polymer.

Intermolecular interactions and crystal-field effects result mainly in the broadening of the valence structures in the solid phase. Finally, the study of the similar valence spectra of polyethylene, graphite, and diamond reveals that the density of states is not appreciably affected by long-range order in the crystal, the fundamental structures of the valence band being determined by the atomic properties and the short-range symmetry of the crystal.

ACKNOWLEDGMENTS

The authors wish to thank their colleagues from Namur, Professor J. Verbist and J. Riga, and from Uppsala, Professor K. Siegbahn and Dr. U. Gelius for stimulating discussions. One of us (J.J.P.) is grateful to the FNRS (Belgium) for financial support.

---

*Aspirant du Fonds National belge de la Recherche Scientifique.

[1] (a) K. Siegbahn *et al.*, *ESCA* (Almqvist and Wiksells, Uppsala, 1967); (b) K. Siegbahn *et al.*, *ESCA Applied to Free Molecules* (North-Holland, Amsterdam, 1969); (c) K. Siegbahn, in *Electron Spectroscopy, Progress in Research and Applications*, edited by R. Caudano and J. Verbist (Elsevier, Amsterdam, 1974), p. 5.

[2] M. G. Mason and R. C. Baetzold, J. Chem. Phys. 64, 271 (1976).

[3] J. J. Pireaux, S. Svensson, E. Basilier, *P*-Å Malmqvist, U. Gelius, R. Caudano, and K. Siegbahn, Phys. Rev. A 14, 2133 (1976).

[4] J. J. Pireaux, Ph.D. thesis (Facultés Universitaires, Namur, 1976) (unpublished).

[5] K. Siegbahn, D. Hammond, H. Fellner-Feldegg, and E. F. Barnett, Science 176, 245 (1972).

[6] G. Johansson, J. Hedman, A. Berndtsson, M. Klasson, and R. Nilsson, J. Electron. Spectr. 2, 295 (1973).

[7] J. Delhalle, J. M. André, S. Delhalle, J. J. Pireaux, R. Caudano, and J. J. Verbist, J. Chem. Phys. 60, 595 (1974).

[8] P. H. Citrin and D. R. Hamann, Chem. Phys. Lett. 22, 301 (1973).

[9] R. A. Holroyd and R. L. Russel, J. Phys. Chem. 78, 2118 (1974).

[10] Eastman Organic Chem. Bull. 47, 1 (1975).

[11] (a) M. Fujihira and H. Inokuchi, Chem. Phys. Lett. 17, 554 (1972); (b) K. J. Less and E. G. Wilson, J. Phys. C 6, 3110 (1973); (c) D. K. Davies, *Static Electrification* (Institute of Physics and Physical Society, London, 1976), Conf. Ser. No. 4, p. 29.

[12] R. Hoffman, J. Chem. Phys. 40, 2047 (1963).

[13] Reference 1b, Appendix D.

[14] J. J. Pireaux, Appl. Spectr. 30, 219 (1976).

[15] J. M. André, J. Delhalle, S. Delhalle, R. Caudano, J. J. Pireaux, and J. J. Verbist, Chem. Phys. Lett. 23, 206 (1973).

[16] R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, Phys. Rev. B 13, 1396

(1976).

[17] A. Hoareau, P. Joyes, B. Cabaud, and R. Uzan, Surf. Sci. 57, 279 (1976), and references therein.

[18] (a) R. G. Cavell, S. P. Kowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, Phys. Rev. B 7, 5313 (1973); (b) F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Cavell, R. A. Pollak, and D. A. Shirley, *ibid*. 9, 5268 (1974).

[19] J. Delhalle, S. Delhalle, and J. M. André, Chem. Phys. Lett. 34, 430 (1975).