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# Densities of States in Particles and Crystals: Characterization of Bulk and Surface Properties

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# Densities of states in particles and crystals: characterization of bulk and surface properties

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This paper is concerned with the restrictions that local symmetry requirements impose on the structures of model clusters chosen for the reproduction of electronic structure, as densities of states, in metals. Simple techniques for the identification of such local symmetries from wave vector group symmetries are outlined. The theory is applied to iridium and comparisons are made between the calculated and measured dialectric function related to the reflectivity of the metal.

## INTRODUCTION

The recently developed spherical shell method (Quinn *et al.* 1983, 1984*a*, *b*, *c*; Redmond *et al.* 1983) is an efficient method by which to catalogue the wavefunctions of a system as symmetry types when the system structure can be described by using point group theory. Individual particles in powder catalysts and single crystals of the dimensions used in modern surface-monitoring instruments such as electron spectrometers are large ensembles of atoms for which this type of analysis permits unusual connections between band structure, based on space group theory, and molecular orbital theory, based on point group theory, to be made. In particular, comparisons can be made between the local properties as local densities of states, of lattice sites in surface or bulk regions or such materials that are basic to the interpretation of experimental data and theoretical models. In this paper this approach is shown to lead to a basis for the modelling of Brillouin zone electronic structure in metals and the reproduction of aspects of the optical properties of such material by using small metal-atom clusters when the essential symmetry criteria are complied with within these clusters. Group theory criteria for the reproduction of bulk electronic structure in calculations using clusters are also assessed.

## SYMMETRY-BASED LOCAL DENSITIES OF STATES IN CLUSTERS

In the ideal crystalline model (Quinn 1973) lattice points are identified by the general translational vector $\boldsymbol{R}_{mnp}$ such that

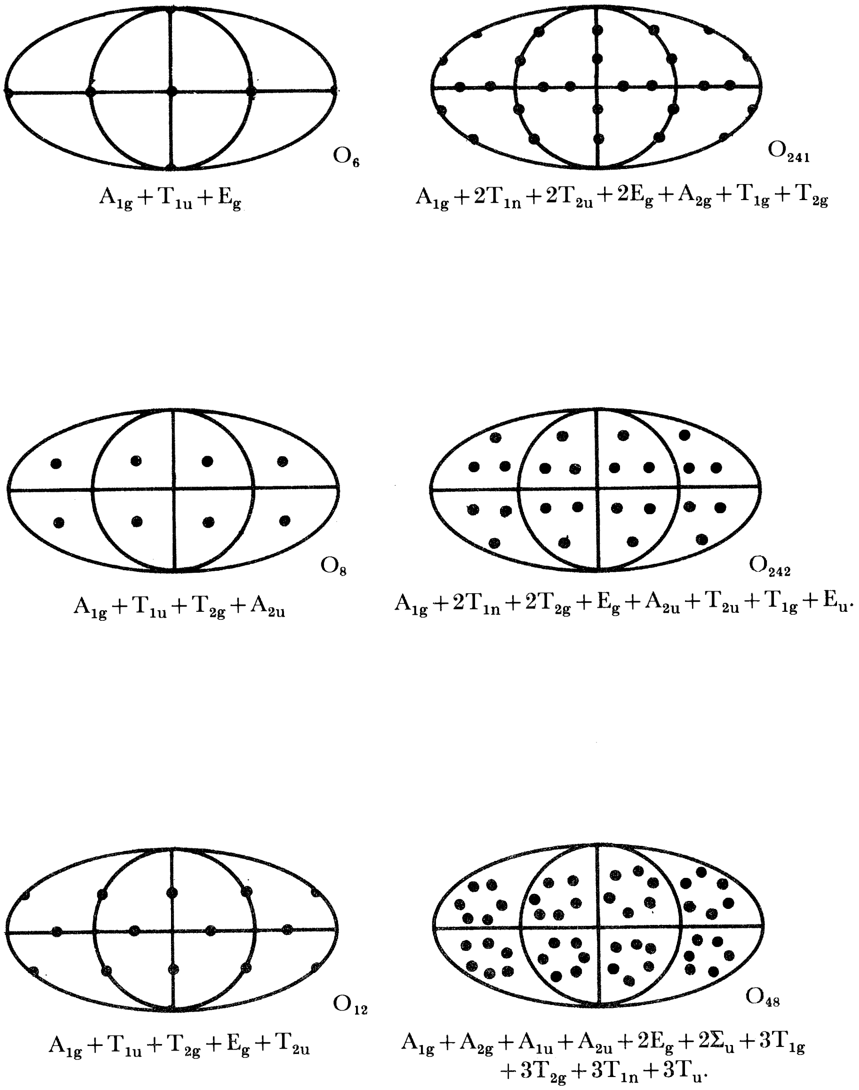
$$\boldsymbol{R}_{mnp} = m\boldsymbol{a} + n\boldsymbol{b} + p\boldsymbol{c}. \tag{1}$$

In cubic systems $|\boldsymbol{a}| = |\boldsymbol{b}| = |\boldsymbol{c}|$ and define the conventional unit cell edge. For b.c.c. and f.c.c. arrays the $m$, $n$ and $p$ parameters can be other than integers and half integers subject to restrictions similar to the extinction rules on Miller indices. For the primitive cubic array of cubium any integer $\{mnp\}$ set is allowed.

Within the spherical shell method each $\{mnp\}$ set for a particular array defines an orbit of the structure considered to be generated by the shells of lattice positions identified by $|\boldsymbol{R}_{mnp}|$

about the coordinate origin. For a 'surfaceless' ideal crystalline array the local site symmetry in cubic arrays is always $O_h$ for any choice of origin. In real cubic crystals, the crystalline array is truncated by the presence of the surface interface, and so the local site symmetry is reduced to the symmetry of the appropriate dihedral point group, which takes account of any surface reconstruction or the presence of absorbed layers.

The determination of a symmetry-based density of states for any site in an array is then a straightforward exercise in the solving of the three-square problem of (1) (McKiernan 1984), which gives the relevant $\{mnp\}$ and so the total numbers of each kind of irreducible



$O_6$: $A_{1g}+T_{1u}+E_g$

$O_{241}$: $A_{1g}+2T_{1n}+2T_{2u}+2E_g+A_{2g}+T_{1g}+T_{2g}$

$O_8$: $A_{1g}+T_{1u}+T_{2g}+A_{2u}$

$O_{242}$: $A_{1g}+2T_{1n}+2T_{2g}+E_g+A_{2u}+T_{2u}+T_{1g}+E_u$.

$O_{12}$: $A_{1g}+T_{1u}+T_{2g}+E_g+T_{2u}$

$O_{48}$: $A_{1g}+A_{2g}+A_{1u}+A_{2u}+2E_g+2\Sigma_u+3T_{1g}+3T_{2g}+3T_{1n}+3T_u$.

FIGURE 1. The six distinct orbits ($O_6 \ldots O_{48}$) of the group $O_h$ as Mollweide projections, which occur on concentric spherical shells for the lattice sites of cubic arrays. The radial parameter $R$ of (1) defines each shell and the distinct orbits on any shell are identified by the distinct $\{mnp\}$. The Mollweide projections are drawn for the unit sphere and a right-handed coordinate system with $\pm Z$ at the north and south poles, $\pm X$ at the centre and extreme left *and* right-hand equatorial positions and $\pm Y$ at the intermediate right and left-hand intersections of the $+Z, +Y, -Z, -Y$ great circle with the equatorial great circle. The direct-sum irreducible components of each orbit's permutation representation is given beneath each projection.

representation of the site point group in a system of a given size, i.e. given number of orbits or radius $R_{mnp}$ (Quinn *et al.* 1984*c*; Quinn 1985). In cubic arrays it is found that only six distinct kinds of orbit are allowed. These are shown in figure 1 as lattice positions on a spherical shell. Each such orbit in an array about a given site contributes the irreducible components of its permutation representation given to the σ-character of the symmetry-based density of states for the array.

At bulk sites the 48-point orbit $O_{48}$ and the corresponding regular representation of the array point group dominate. This result (Quinn *et al.* 1984*c*; Quinn 1985) for clusters formed as cubical arrays of sufficient size makes a first connection between the point group analysis and conventional space group theory. The 48-dimensional irreducible representations of semidirect product cubic space groups are associated with general points of the structure Brillouin zone and the 48-point stars of the general wave vectors. The density of such general points is much higher than the density of special points and so the numbers of 48-dimensional representations of the point group $O_h$ subduced are much greater.

## THE σ-CHARACTER AND THE ELECTRONIC STRUCTURES OF ‘CUBIUM’ CLUSTERS

The σ-character of the symmetry-based density of states especially is interesting for the cubium array. The σ-character is the s-character also and so relates directly to the densities of states at bulk or near-surface sites in cubium, or large clusters of s-orbitals in primitive cubic array chosen to model the bulk hypothetical lattice. In figure 2 local electronic densities of states are calculated by using the recursion method (Kalkstein & Soven 1971; Haydock & Kelly 1973) for cubium and using its equivalent in the molecular orbital theory for clusters, the simple Hückel calculation for a cube of 729 s-orbitals (Messmer 1977) are given for surface and near-surface sites. The agreement between the cluster calculation and that for the semi-infinite solid is striking and suggests that both bulk and surface local densities of states are reproduced very well in the cluster calculation.

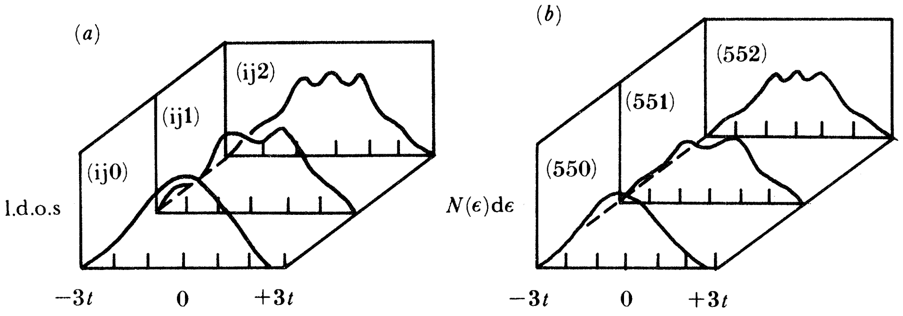


FIGURE 2. Local densities of electronic states at surface and subsurface sites in (*a*) cubium (Kalkstein & Soven 1971) and (*b*) a 9 × 9 × 9 cluster of s-orbitals (Messmer 1977).

In table 1 the symmetry-based densities of states are given for various $O_h$ clusters up to large clusters containing many millions of s-orbitals in primitive array. These data would suggest that bulk properties of the electronic structure of cubium are not represented well by even large clusters of many thousands of s-orbitals since the density of states distribution remains significantly different from the regular representation criterion characteristic of bulk sites. The success of the cluster calculation is difficult to explain given the group theoretical data. The cube geometry divides the system structure into three regions of different symmetries: the inner region about the origin, including all the sites for which the local densities are calculated, of complete $O_h$ orbits; the intermediate surrounding region of incomplete $O_h$ orbits; and the vacuum beyond the cube surface. Such breaking of the symmetry has been suggested to be useful (Heine 1980) in the modelling of bulk structure by using cluster calculations. But in the cube formed by the $9 \times 9 \times 9$ array of s-orbitals the local densities of states on the sites chosen cannot include other than contributions from the most symmetric wavefunctions of the cluster. Even including all the cube wavefunctions for the $C_{4v}$ structure as a whole, significant variations for the $C_{4v}$ regular representation remain in the symmetry-based densities of states. Moreover, individual lattice sites in the cube cannot contribute to certain wavefunctions of the system, in contrast to the situation with the semi-infinite structure in which all lattice sites are equivalent.

Table 1. Symmetry-based densities of states for cubium clusters

($R$ is the cluster radius in unit cell edges; $S$ is the shell number; $N$ is the number of occurrences of each irreducible representation of $O_h$ listed by using Mulliken symbols. $A$ is the number of s-orbitals in each cluster.)

| | $R = 2$<br>$S = 4$<br>$A = 33$ | | $R = 6$<br>$S = 31$<br>$A = 925$ | | $R = 10$<br>$S = 85$<br>$A = 4169$ | | $R = 50$<br>$S = 2085$<br>$A = 523305$ | | $R = 80$<br>$S = 5335$<br>$A = 2.14$ M | | $R = 160$<br>$S = 21335$<br>$A = 17.16$ M | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| IR | $N$ | (%) | $N$ | (%) | $N$ | (%) | $N$ | (%) | $N$ | (%) | $N$ | (%) |
| $A_{1g}$ | 5 | 31.25 | 42 | 10.74 | 143 | 8.19 | 12124 | 5.56 | 47748 | 5.35 | 369651 | 5.17 |
| $T_{1u}$ 1 | 4 | 25.00 | 41 | 10.49 | 142 | 8.13 | 12124 | 5.56 | 47748 | 5.35 | 369651 | 5.17 |
| $T_{2g}$ 1 | 2 | 12.50 | 35 | 8.95 | 132 | 7.56 | 12074 | 5.54 | 47668 | 5.34 | 369491 | 5.17 |
| $E_g$ 1 | 3 | 18.75 | 38 | 9.72 | 137 | 7.85 | 12096 | 5.55 | 47702 | 5.34 | 369559 | 5.17 |
| $A_{2u}$ | 1 | 6.25 | 22 | 5.63 | 94 | 5.38 | 11101 | 5.09 | 45170 | 5.06 | 359467 | 5.03 |
| $T_{1u}$ 2 | 0 | 0.00 | 28 | 7.16 | 120 | 6.87 | 012011 | 5.51 | 47566 | 5.33 | 369286 | 5.17 |
| $T_{2u}$ 1 | 1 | 6.25 | 32 | 8.18 | 127 | 7.27 | 12046 | 5.52 | 47622 | 5.33 | 369399 | 5.17 |
| $E_g$ 2 | 0 | 0.00 | 15 | 3.84 | 77 | 4.41 | 10692 | 4.90 | 44131 | 4.94 | 355303 | 4.97 |
| $T_{1g}$ 1 | 0 | 0.00 | 28 | 7.16 | 120 | 6.88 | 12011 | 5.51 | 47566 | 5.33 | 369286 | 5.17 |
| $T_{2g}$ 2 | 0 | 0.00 | 19 | 4.86 | 89 | 5.10 | 11073 | 5.08 | 45124 | 5.05 | 359375 | 5.03 |
| $E_u$ 1 | 0 | 0.00 | 19 | 4.86 | 89 | 5.10 | 11073 | 5.08 | 45124 | 5.05 | 359375 | 5.03 |
| $T_{1u}$ 3 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $T_{2u}$ 2 | 0 | 0.00 | 15 | 3.84 | 77 | 4.41 | 10692 | 4.90 | 44131 | 4.94 | 355303 | 4.97 |
| $A_{2g}$ | 0 | 0.00 | 15 | 3.84 | 77 | 4.41 | 10692 | 4.90 | 44131 | 4.94 | 355303 | 4.97 |
| $T_{1g}$ 2 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $T_{2g}$ 3 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $E_u$ 2 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $T_{2u}$ 3 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $T_{1g}$ 3 | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |
| $A_{1u}$ | 0 | 0.00 | 6 | 1.53 | 46 | 2.63 | 9754 | 4.47 | 41689 | 4.67 | 345392 | 4.83 |

## BRILLOUIN ZONE BAND-STRUCTURE COMPONENTS AND CLUSTER CALCULATIONS: OPTICAL PROPERTIES

Certain aspects of bulk densities of states do appear to be representable by using small clusters as long as the cluster properties as a whole are considered and the symmetry requirements are met with each atomic position equivalent. The spherical-shell technique provides a very simple procedure by which one can go from the irreducible representations of the wave vector groups in the Brillouin zone to the representations of the space group subduced in the local site point groups the symmetries relevant to local densities of states, without the need to evaluate the 'allowability' (Bouckaert *et al.* 1936) of the wave vector group representations. For the semi-direct product space groups the totally symmetric irreducible representation of each wave vector group $L_k$ (II) (Quinn 1973) generates the permutation representation appropriate to its star of k and therefore the σ- or s-character component of a bulk site local density of states. From the $\Gamma_\sigma$-character the p- and d-characters ($\Gamma_p$ and $\Gamma_d$) follow directly through the relations

$$\Gamma_p = \Gamma_\sigma + \Gamma_\pi = \Gamma_{xyz} \otimes \Gamma_\sigma, \tag{2}$$

$$\Gamma_d = \Gamma_\sigma + \Gamma_\pi + \Gamma_\sigma = \Gamma_{xyz} \otimes \Gamma_\pi - \epsilon \Gamma_\sigma, \tag{3}$$

where $\Gamma_\pi$ and $\Gamma_\sigma$ are the characters of σ and δ oriented interactions about the bulk site and $\epsilon$ is the antisymmetrizing character of the point group (in $O_h \epsilon = A_{1u}$), (Redmond *et al.* 1984).

For the three important symmetry directions ΓX, ΓK and ΓL of the Brillouin zone of f.c.c. metals, the band structure components are locally, about a bulk site, the irreducible representations of $O_h$ given in table 2. A comparison of these data with the data given in figure 1 and (2) and (3) reveals that the six, eight and twelve membered orbits of the cubic array for transition metal clusters contributing valence s, p and d orbitals at each orbit site contain all the symmetries of wavefunction required for the ΓX, ΓK and ΓL band structure.

TABLE 2. LOCAL SYMMETRIES OF BAND STRUCTURE COMPONENTS TRANSFORMING AS THE IRREDUCIBLE REPRESENTATIONS OF WAVE VECTOR GROUPS OF THE CUBIC SPACE GROUPS SYMMETRY LINES ΓX, ΓL, ΓK

(The symmetries are the permutation representations of the star of k in each case. The p and d, $\pi + \delta$ symmetries follow from (2) and (3).)

| Brillouin zone symmetry | direction | σ-rep | π-rep | δ-rep |
|---|---|---|---|---|
| Δ | (100) | $A_{1g} + T_{1u} + E_g$ | $T_{1u} + T_{1g}$<br>$+ T_{2u} + T_{2g}$ | $A_{2g} + A_{2u} + E_g$<br>$+ E_u + T_{2g} + T_{2u}$ |
| Λ | (111) | $A_{1g} + T_{1u} + T_{2g}$<br>$+ A_{2u}$ | $T_{1u} + T_{1g} + T_{2u}$<br>$+ T_{2g} + E_g + E_u$ | $T_{1u} + T_{1g} + T_{2u}$<br>$+ T_{2g} + E_g + E_u$ |
| Σ | (110) | $A_{1g} + T_{1u} + E_g$<br>$+ T_{2g} + T_{2u}$ | $A_{2g} + A_{2u} + 2T_{1u}$<br>$+ 2T_{2u} + T_{1g}$<br>$+ T_{2g} + E_g + E_u$ | $A_{1g} + A_{1u} +$<br>$T_{1u} + T_{1g} +$<br>$2T_{2u} + 2T_{2g}$<br>$+ E_g + E_u$ |

The band structure to high energy for iridium metal has been determined recently by using the KKR (Korringa, Kohn and Rostocker) method (Ray *et al.* 1983). The ΓX, ΓK and ΓL sections of this band structure are reproduced in figure 3 and these data have been converted to density of states data in figures 4, 5 and 6, wherein the density of states profiles from extended Hückel calculations on $Ir_6$, $Ir_8$ and $Ir_{12}$ $O_h$ clusters are also given. The extended Hückel calculations have been made for the geometries of the cluster atoms separated by the experimental bond distance, 270.79 pm, the experimental v.s.i.e. parameters for 5d, 6s and 6p states determined by Bleiber (quoted in Bartel *et al.* 1984), and the wavefunctions of Fitzpatrick & Murphy (1984). The extended Hückel densities of states data in the diagrams were obtained by broadening the discrete energy levels by using a Gaussian parameter equal to 0.3 and the lowest energy level of each cluster was matched to the bottom of the Ir valence band. It is to be emphasized that in the clusters chosen each site contributes to the wavefunction symmetries in exactly the manner required in the bulk. For this reason the clusters do not include atomic sites centred at the origins of the clusters. Such sites would be like many of the sites in the $9 \times 9 \times 9$ cubium cluster already discussed and deficient in their capacities to make contributions to certain cluster wavefunctions.

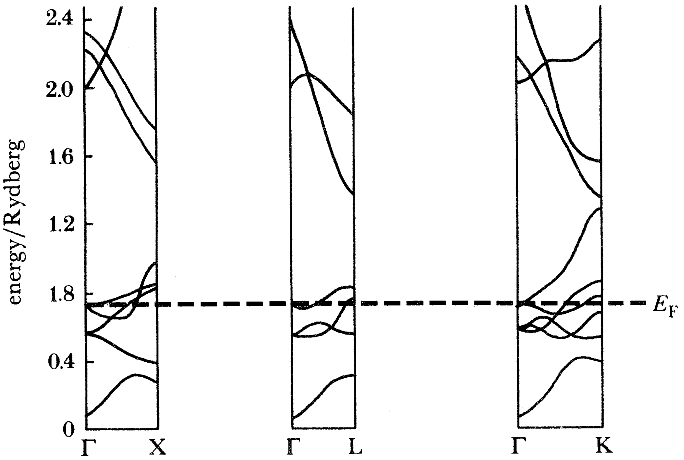


FIGURE 3. Band structure along ΓX, ΓK and ΓL symmetry lines in iridium metal to high energy (Ray *et al.* 1983).

A considerable degree of similarity exists between the densities of occupied states and d-band widths in the band structure and the gaussian broadened extended Hückel calculations. Moreover, some correspondence can be discerned also between prominent features of the unoccupied states determined by both procedures, which are of particular importance in the interpretation of optical properties and electron spectroscopic data.

Several studies of the optical properties of Ir have been made (Hass *et al.* 1967; Kirillora *et al.* 1972; Weaver *et al.* 1974; Weaver 1975; Weaver *et al.* 1977). The imaginary part ($\epsilon_2$) of the complex dielectric function extracted from reflectivity measurements is a parameter that can be compared with calculated values from band structure data. The energy distribution of the joint densities of states in the constant matrix approximation relates to $\epsilon_2$ through the expression

$$\omega^2\epsilon_2 \propto \sum_{ij} \int \mathrm{d}^3k\,\delta(E_{\mathrm{F}}(\boldsymbol{k}) - E_i(k) - \hbar\omega). \qquad (4)$$

In figure 7 the calculated e.d.j.d.o.s. obtained from the cluster calculations are compared with the $\epsilon_2$ data obtained from experiment. The important experimentally observed features are identifiable in the data from the cluster calculations. At low photon energies the main feature in the $\epsilon_2$ spectrum is found at *ca.* 1.0 eV and correlates well with the prominent ΓX-related feature of the cluster calculations. In the intermediate region of photon energy between 4 and 20 eV, again the main structure in the $\epsilon_2$ spectrum appears to be associated with transitions around the ΓX line in the Brillouin zone and both these conclusions agree with the assignments made on the basis of band-structure data (Ray *et al.* 1983).

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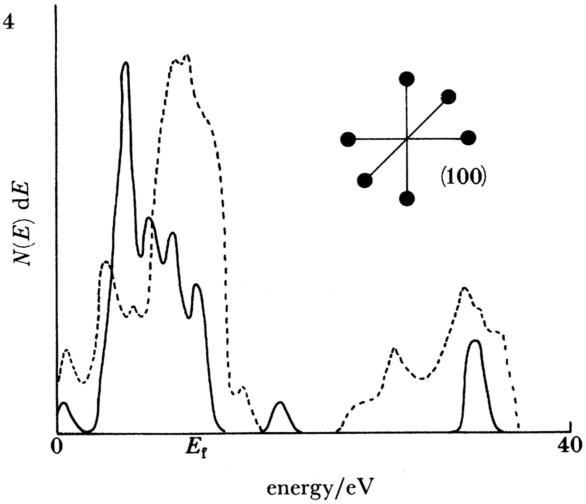

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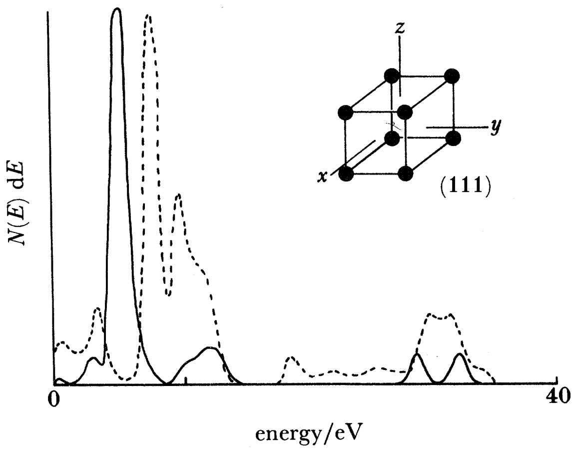

FIGURE 4. Densities of states from band structure (Ray *et al.* 1983) along ΓX (solid line) and for $Ir_6$ (broken line) by using extended Huckel Theory.

FIGURE 5. Same as figure 4 but along ΓL and for $Ir_8$.

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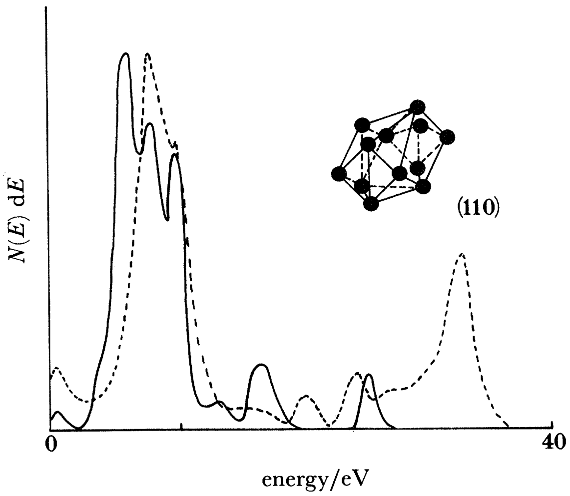

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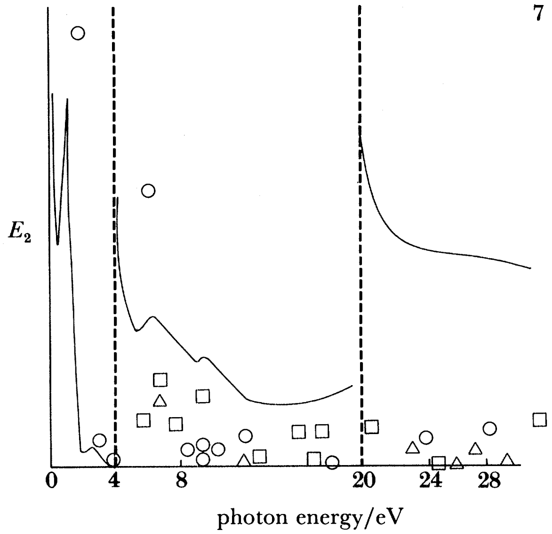

FIGURE 6. Same as figure 4 but along ΓK and for $Ir_{12}$.

FIGURE 7. Imaginary part ($E_2$) of dielectric function in Iridium: solid lines from reflectivity measurements; ○ from $Ir_6$ joint density of states (equation (4)); △ from $Ir_8$; □ from $Ir_{12}$.

## CONCLUSIONS

The role of group theory in the modelling of bulk crystal electronic structure by using clusters has been assessed in this paper. It has been shown that band structure can be reproduced successfully by using small clusters when the symmetry requirements of the bulk and model systems are matched. Given the unrefined nature of the calculations presented here the agreement between the results based on the cluster models and the band structure data is very encouraging for future work. The electronic structure of Ir along the ΓX, ΓK and ΓL directions of the crystal Brillouin zone obtained from the cluster calculations has been shown to fit very well with the band structure along these symmetry directions and also to be compatible with the main features of the dielectric function spectrum for the metal. A simple technique facilitating the generation of local site symmetries from wave vector group symmetries has been presented.

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