

## Charge transfer and the nature of empty states in potassium-intercalated graphite

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The near-edge photoabsorption spectra of graphite intercalation compounds of potassium have been measured at the energy corresponding to the  $K$  edge of potassium. Polarization of a synchrotron beam has been used to probe the local symmetry of empty states at the potassium site. As a result, peaks in the spectra for  $\text{KC}_8$  have been identified with the transitions to final states provided by our energy-band-structure calculation. These results along with the calculated wave functions demonstrate the hybridization between carbon and potassium orbitals in the empty bands of  $\text{KC}_8$ . The charge transfer between potassium and graphite layers is estimated from the measurements and supported by the calculations.

The graphite intercalation compounds (GIC's) are formed from a regular stacking of  $n$  graphite sheets between two intercalant (foreign atoms or molecules) layers.  $n$  defines the stage of the compound. Thus, the first stage is composed of alternate layers of graphite and intercalant. When the intercalated species are alkali-metal atoms, they act as donors, i.e., they contribute a portion of their outer electron to graphite layers. Original attempts<sup>1</sup> to explain the properties of these materials assumed that the alkali-metal atom has no effect on the electronic structure of graphite and simply donates charge to each graphite layer (rigid-band model). By our theoretical and experimental studies of the ground-state charge and momentum density of graphite, lithium, and potassium GIC's,<sup>2-7</sup> we have demonstrated the failure of this model. Our results indicate that the carbon states substantially hybridize with those of potassium, leading to a distortion of the graphite charge density and a resulting modification of its band structure. This hybridization has also been observed by Hague *et al.*<sup>8</sup> in x-ray photoemission spectroscopy (XPS) studies of this compound.

The detailed nature of the empty states and the related question of "charge transfer" between the intercalant and graphite layers in the first-stage  $\text{KC}_8$  are important questions that have not yet been clearly resolved. Energy-band calculations offer two models predicting substantially different charge transfer.<sup>6,9</sup> Experimental results so far have been interpreted to support one or the other of these models.<sup>8,10-13</sup> In the present work, we have employed x-ray-absorption near-edge polarization-dependent structures (XANEPS) measurements on  $\text{KC}_8$ , at the potassium  $K$  edge, along with the calculated energy bands for  $\text{KC}_8$ , in order to answer these questions definitively. In such spectroscopy, when the transitions originate from the  $s$  core levels, selection rules for the dipole transition limit the final states to those with  $p$  character at the specific site. These measurements, using linearly polarized light,

offer a site-specific probe of the symmetry of empty-state wave functions, and this is particularly suitable for GIC's as we shall see. In pristine graphite, if the electric field  $\mathbf{E}$  of linearly polarized light lies within the layers, coupling is only made to  $\sigma$  bands (a mixture of  $p_x$  and  $p_y$  final states, here after referred to as  $p_{xy}$ ). But if the electric field  $\mathbf{E}$  is perpendicular to the graphite planes, transitions will only be allowed to  $\pi$  bands ( $p_z$  states).<sup>14</sup> Similarly, in potassium-intercalation compounds, the wave functions have purely  $p_{xy}$  or  $p_z$  symmetry, but not both. Since the transitions originate from the potassium  $1s$  level, only the symmetry of the final state at a potassium site is relevant. This permits the study of hybridization between K and C orbitals in the unoccupied states.

All samples are synthesized from highly oriented pyrolytic graphite (HOPG) using the two-zone furnace method,<sup>15</sup> kept in dry argon at all times, and characterized by x-ray diffraction. The thickness of each sample is uniform, depending on the stage, and is chosen in order to optimize the statistics in these transmission measurements (18  $\mu\text{m}$  in the case of  $\text{KC}_8$ ). The experiments were carried out at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE), using the linearly polarized synchrotron beam. A two-crystal Si(111) monochromator provides an x-ray beam tunable around the energy of the  $K$  absorption edge of potassium. In this Bragg reflection, the second harmonic is practically absent in the monochromatic beam. Two uncoated glass mirrors are used to reject the remaining harmonics with a rejection ratio of  $10^{-4}$  at this energy range<sup>16</sup> (3.6 keV). The polarization ratio of the monochromatized beam is better than 99%. This high ratio is obtained by using a sharply collimated white beam coming from the central part of the photon source and a vertical scattering plane for the monochromator. The polarization angle  $\theta$  is defined as the angle between the electric field  $\mathbf{E}$  and the normal to the sample, i.e., the  $c$  axis (Fig. 1). The angle  $\theta$

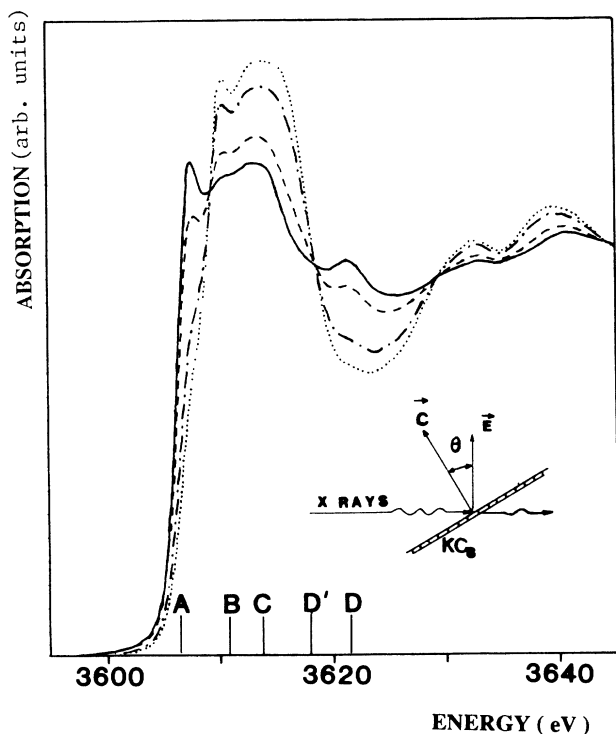


FIG. 1. Experimental XANEPS spectra of  $\text{KC}_8$  at the potassium  $K$  edge for various angles  $\theta$ :  $90^\circ$  (solid line);  $60^\circ$  (dashed line);  $30^\circ$  (dashed-dotted line). The spectrum at  $\theta=0^\circ$  (dotted line) is obtained by extrapolation from results at other values of  $\theta$ . The peak energies are marked by lines at the bottom of the figure.

is varied between  $90^\circ$  and  $30^\circ$  in  $15^\circ$  steps. For each value of  $\theta$ , the spectrum of the transmitted photons through the sample is recorded in the energy range 3580–3700 eV in 0.15-eV steps. The total resolution is 1 eV, due to the convolution of the 0.5-eV core-level width<sup>17</sup> with the 0.85-eV experimental resolution.<sup>18</sup> Since the effective thickness of the sample varies with  $\theta$ , experimental spectra are matched at 70 eV beyond the edge. In view of the thickness of the sample and since the strength of the transmitted beam is larger than 10% of the incident, this is truly a bulk measurement.

If a peak in the spectrum is due to transitions to final states with only  $p_{xy}$  content, it decreases in strength with decreasing  $\theta$  and disappears at  $\theta=0^\circ$ . The opposite behavior is obtained with  $p_z$  content. If, in the energy range of interest, there are two sets of final states, one having  $p_z$  character and the other  $p_{xy}$ , for each energy  $E$  the absorption coefficient  $\mu(E, \theta)$  varies with  $\theta$  as

$$\mu(E, \theta) = \mu_{xy}(E) \sin^2 \theta + \mu_z(E) \cos^2 \theta,$$

where  $\mu_{xy}(E)$  and  $\mu_z(E)$  are absorption coefficients for dipolar transitions  $1s \rightarrow p_{xy}$ ,  $1s \rightarrow p_z$ , respectively. Even though the measurements were carried out on samples synthesized from HOPG, all the microcrystals have parallel  $c$  axes. Thus, dependence of the spectra on the polarization angle  $\theta$ , defined in a plane containing the  $c$

axis, is the same as for a single crystal. Due to the geometry of the samples and the experimental setup, values of the angle  $\theta$  less than  $30^\circ$  could not be reached. Thus, the  $\theta=0^\circ$  spectrum (beam perpendicular to the  $c$  axis) is obtained by the linear extrapolation of the five measured spectra ( $\theta=90^\circ, 75^\circ, 60^\circ, 45^\circ$ , and  $30^\circ$ ) as a function of  $\cos^2 \theta$ .

We have used our calculations<sup>6</sup> to identify the origin of structures in  $\text{KC}_8$  spectra (Fig. 1). The self-consistent-field energy-band structure was obtained using *ab initio* norm-conserving pseudopotentials,<sup>19</sup> and the wave functions were expanded in a mixed basis set of plane waves and localized orbitals.<sup>20</sup> The localized parts of the final wave functions are used to obtain information about their content and symmetry at each atomic site. The nonorthogonality of the basis renders exact assignment of weight to the local part difficult. Nevertheless, one can relate the potassium  $p$  content of the wave function to the corresponding coefficients in its expansion, and indicate whether there is strong, weak, or none of a given component. This information is shown in Fig. 2 as a partial band structure for states at and above the Fermi level. It contains only information about the  $p$  content at the potassium site and the density of states for these bands. The final states are clearly confined to well-identified energies in the range of approximately 12 eV above the Fermi level. However, the situation becomes unclear beyond this energy range, due to the large number of overlapping energy bands.

If a peak corresponding to a certain symmetry of final states is experimentally observed, a significant amount of final states of this symmetry has to be present in the calculated partial energy-band structure at this energy (Fig. 2). By the word “amount” we refer to a combination of high density of states and large  $p$  component in decomposition of the wave functions. However, mere existence of states of a certain symmetry in the calculated bands does not necessarily lead to an experimentally observable peak. This can be due to either weak transition probability or overlapping in energy with a structure of the other symmetry.

The first peak,  $A$ , becomes weaker as  $\theta$  decreases but does not disappear at  $\theta=0^\circ$ ; it is still seen as a change of slope on the low-energy side of peak  $B$  (Fig. 1), indicating transitions to both  $p_z$  and  $p_{xy}$  final states at that energy. The  $p_z$  final states correspond to a band (Fig. 2) appearing just above the Fermi level and concentrated mainly in the center of the Brillouin zone. The  $p_{xy}$  final states can be identified both with a band crossing the Fermi level in the  $\Delta$  direction, which starts with a high  $p_{xy}$  amount at  $Y$  and vanishes when it reaches  $\Gamma$ , and also with a band with a significant  $p_{xy}$  amount in the  $A$  direction. It is particularly important that the Fermi level crosses these bands at a position of a low  $p_{xy}$  amount, precluding the experimental observation of transitions to that level. Thus, the peak  $A$  is placed 1 eV above the Fermi level in Fig. 2. Except at point  $Y$ , in the range of 4 eV above the peak  $A$ , there are only states with very little  $p_{xy}$  content. The reason that these states are not experimentally observed as a clear peak is possibly due to a low-transition probability and because a relatively small region of the Brillouin

loun zone is involved.

The structure noted as *B* can easily be identified with transitions to states at 6 eV above the Fermi level. Both theoretical and experimental results clearly indicate  $p_z$  symmetry. The small width of this peak is consistent with the corresponding small spread in the energy of states contributing to this peak.

The next structure *C* is wider than *B* but has the same behavior with respect to polarization. The situation becomes less certain going to higher energies. However, we notice that a large concentration of states with a  $p_{xy}$  symmetry exists over a wide energy range, in both  $\Delta$  and  $B$  directions and at the  $\bar{K}$  point in the Brillouin zone, leading to the existence of a peak *D* in the measured spectra. Its width is estimated to be at least 3 eV, and the arrow in Fig. 2 indicates the average energy of these states. The change of curvature which occurs between peaks *C* and *D* has been marked as *D'* in Fig. 1. Figure 3 shows the spectra for the first, second, and third stages, measured

for  $\theta=90^\circ$ . The same structures can be identified in all three stages, however, they become narrower in the latter two. The structure *D'* is seen clearly as a peak in the higher stages. This structure is consistent with a  $p_{xy}$  symmetry, both experimentally and theoretically. The reduction in the width of the measured peaks is due to a localization in energy of the potassium content of the  $\pi$  bands as a result of a reduction of the number of potassium nearest neighbors of each carbon atom.

A remarkable feature of the results is that the position of the absorption edge for  $\text{KC}_8$  (as checked with derivative spectra) does not shift more than 0.3 eV from the common value for  $\text{KC}_{24}$  and  $\text{KC}_{36}$ . Based on this, we have developed a model which provides a value for the "charge transfer" in  $\text{KC}_8$ . Peak *A* mainly represents transitions to states above  $E_F$  and is not affected by the lowering of the Fermi level when going from  $\text{KC}_8$  to  $\text{KC}_{24}$ . The only other mechanism for a shift in the position of this peak as a function of stage is a change in ener-

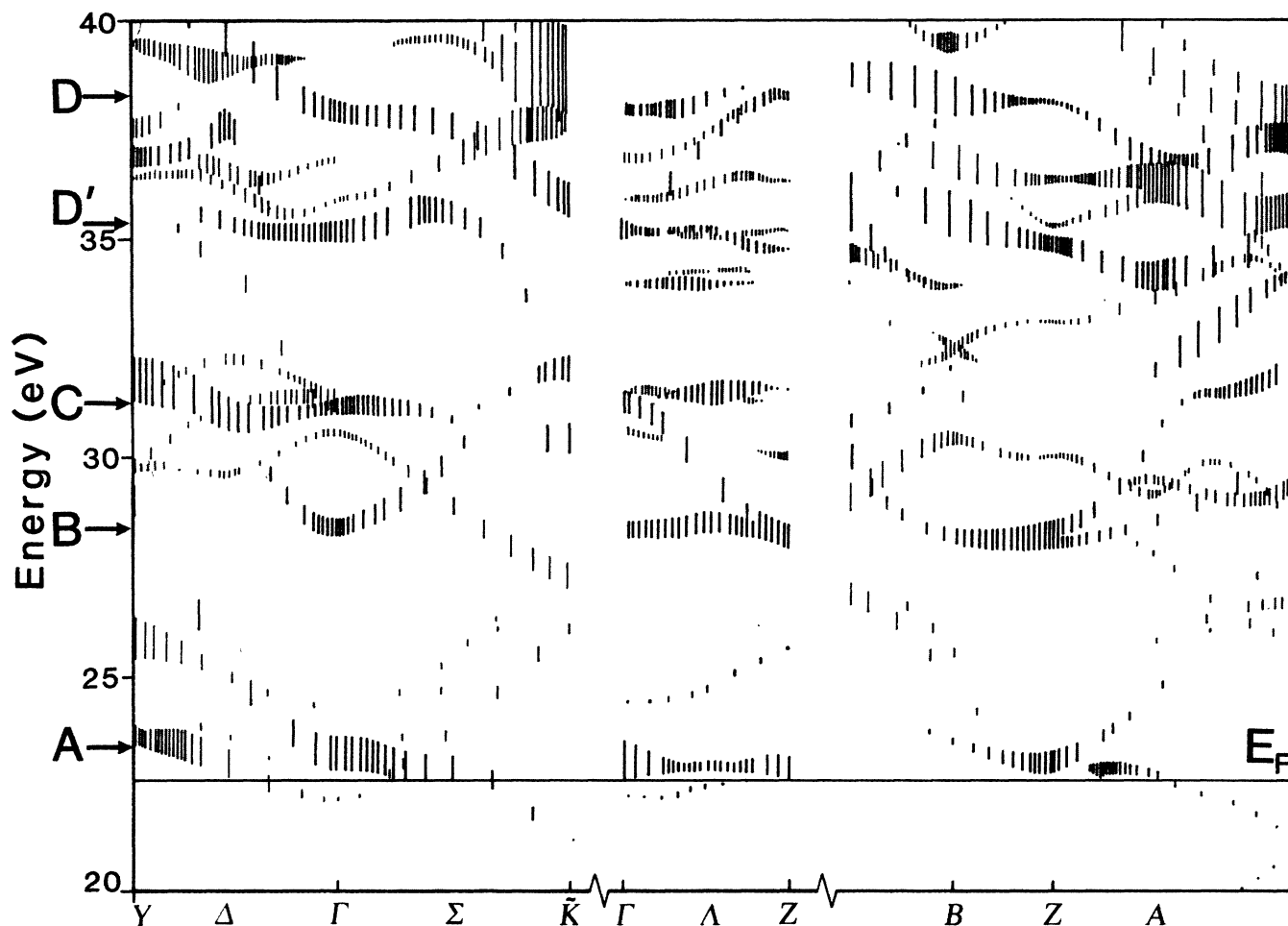


FIG. 2. Partial band structure of  $\text{KC}_8$  ( $p$  content at the potassium site). The height of the bars indicates the weight of the projection of the localized part of the total wave function on the  $l=1$  potassium atomic orbital and their frequency reflects the density of states. Red and black correspond to states of  $p_{xy}$  and  $p_z$  symmetries, respectively.

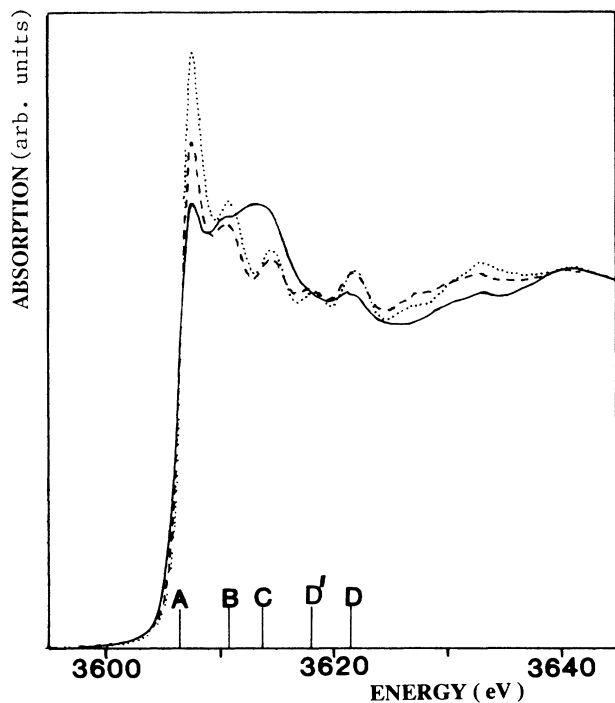


FIG. 3. XANEPS spectra of three stages of potassium intercalated graphite. Solid line:  $\text{KC}_8$ ; dashed line:  $\text{KC}_{24}$ ; dotted line:  $\text{KC}_{36}$ .

gy of both the initial and final states due to a change of screening brought about by charge transfer. We obtain an estimate for the energy shifts of the initial state by a Hartree-Fock-Slater SCF calculation for the  $1s$  state of the potassium ion as a function of its ionicity. The final states for peak *A* correspond to a complex in the potassium GIC's which basically originates from the folding of the unoccupied  $p$  bands of graphite into the Brillouin zone of GIC's, plus a small degree of hybridization with potassium states. Thus, the energy shift of the final states is obtained from the position of  $2s$ - $2p$  complex in the carbon ion as a function of its ionicity. The "cusp" in the energy bands of  $\text{KC}_8$ , located at the  $\bar{K}$  point in the Brillouin zone and at an energy of  $-2$  eV, corresponds to a similar structure in graphite occurring at point  $K$  and defining the position of its Fermi level. Due to the mainly graphitic nature of the  $\pi$  bands, it is reasonable to assume that the position of final states involved in peak *A* will not change with respect to the cusp as we go from stage one to three.

In Fig. 4, we indicate the shifts of the initial and final states with respect to the  $1s$  level of  $\text{K}^0$  and the  $2s$ - $2p$  levels of  $\text{C}^0$  for different values of charge transfer. If we assume that the charge transfer in  $\text{KC}_8$  in total [Fig. 4(a)] as in  $\text{KC}_{24}$  [Fig. 4(b)], the position of the initial state in both compounds will be that of the  $1s$  level of the  $\text{K}^{+1}$  ion, i.e., a lowering of 6.2 eV from the  $1s$  level of  $\text{K}^0$ . The final states for  $\text{KC}_8$  and  $\text{KC}_{24}$  will be at the position of  $2s$ - $2p$  complexes of  $\text{C}^{-1/8}$  and  $\text{C}^{-1/24}$  ions respectively, i.e., raised by 1.2 and 0.4 eV from that of neutral carbon.

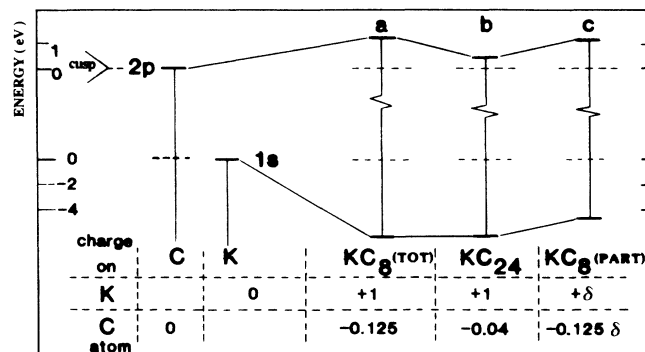


FIG. 4. Position of initial and final states for peak *A* in terms of the corresponding  $K$  and  $C$  ions with different screening: (a)  $\text{KC}_8$ , +1 charge transfer; (b)  $\text{KC}_{24}$ , +1 charge transfer; (c)  $\text{KC}_8$ ,  $+\delta$  charge transfer.

This will require an energy difference of 0.8 eV between the edges of  $\text{KC}_8$  and  $\text{KC}_{24}$ , which would have been easily observed in our experiment. So we must assume that the charge transfer is not total, requiring the initial state in  $\text{KC}_8$  to lie above that of  $\text{KC}_{24}$ , since the ionicity in the former would now be  $\text{K}^{+\delta}$  with  $0 < \delta < 1$  [Fig. 4(c)]. The shifts in the final states correspond to those of  $\text{C}^{-\delta/8}$  and  $\text{C}^{-1/24}$  for  $\text{KC}_8$  and  $\text{KC}_{24}$ , respectively. Calculations were carried out for several values of incomplete charge transfer and it was found that for  $\delta=0.9$ , no shift in the edge would occur between  $\text{KC}_8$  and  $\text{KC}_{24}$ . A shift of 0.3 eV measured from derivatives of Fig. 3 spectra corresponds to  $\delta=0.85$ . This small shift is at the limit of accuracy of our measurement. In contrast, charge transfer of only 50% leads to a shift of 3 eV in the edge towards lower energies, in obvious disagreement with our experimental results. The change in the core-relaxation effect between  $\text{KC}_8$  and  $\text{KC}_{24}$  is assumed to be of second order in this analysis, and the related excitonic effects on peak *A* are assumed to be the same in both compounds.<sup>21</sup> Thus, we estimate the charge transfer to be 0.85. Our measurements are consistent with the value deduced from our energy-band calculation for  $\text{KC}_8$ .

The hybridization between  $K$  and  $C$  brought about by intercalation, also observed in the XPS studies of  $\text{KC}_8$  by Hague *et al.*,<sup>8</sup> has two effects: one is transfer of charge between the intercalant and the carbon layers, and the other is the polarization of carbon charge distribution brought about through interaction with intercalant ions. For this reason, it is difficult to define the charge transfer as a displacement of charge from one species to the other. Such a definition could only be made if there were a unique way to partition the space between the carbon layers and the intercalant. We have defined it in terms of screening of the corresponding atomic energy levels, and obtain a value for charge transfer in terms of an effective ionization of the potassium atom in the solid which would result in the observed behavior of the edge. Moreover, our calculated energy-band structure brings out the

hybridized character of the electronic states of  $KC_8$  and predicts a small fraction of an electron remaining on the potassium site. This is in contrast to other theoretical models that predict a much smaller charge transfer. Furthermore, we have shown that our calculated unoccupied states offer an accurate model for their observed symmetry in XANEPS measurements.

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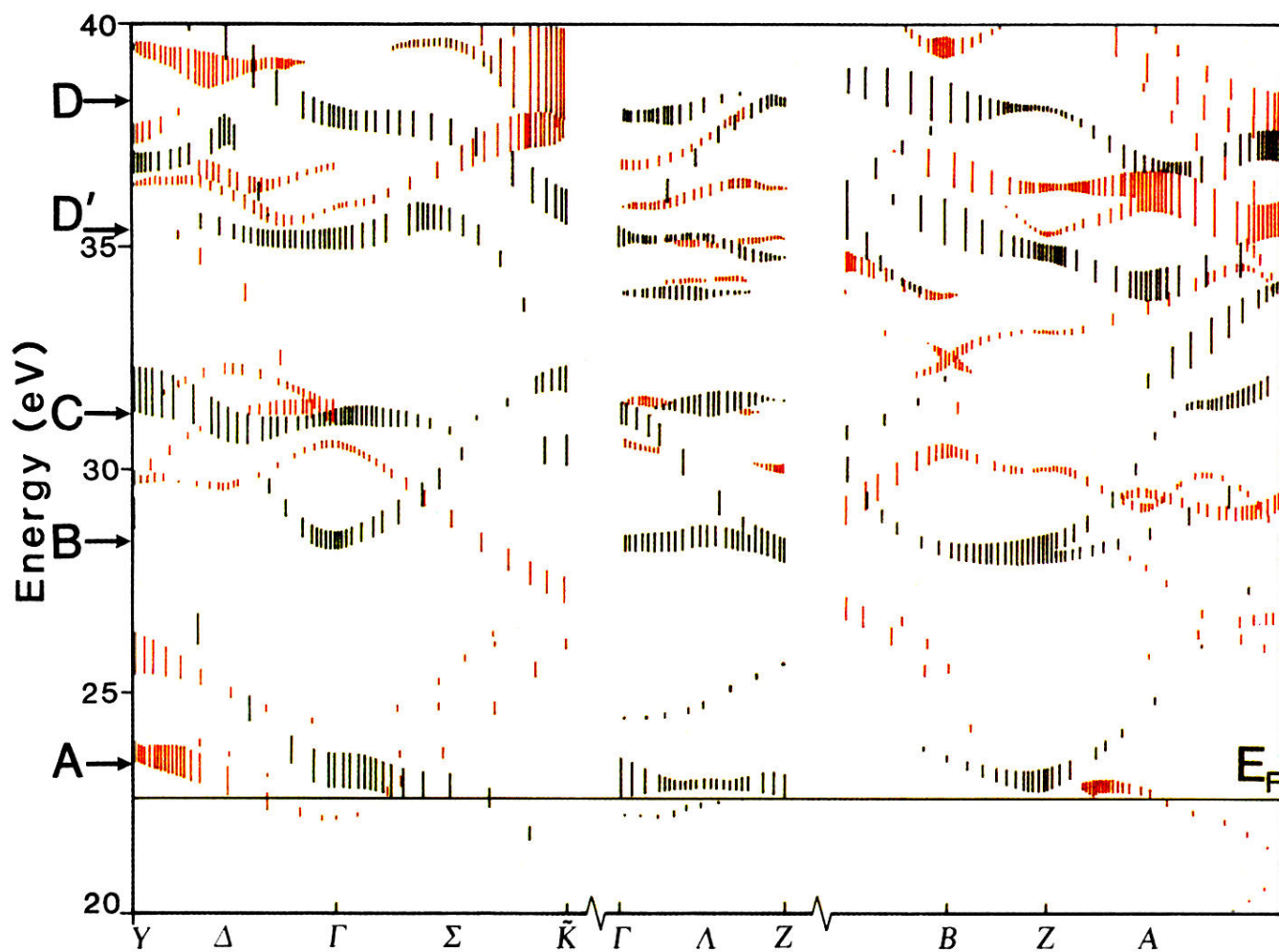


FIG. 2. Partial band structure of KC<sub>8</sub> (*p* content at the potassium site). The height of the bars indicates the weight of the projection of the localized part of the total wave function on the  $l=1$  potassium atomic orbital and their frequency reflects the density of states. Red and black correspond to states of  $p_{xy}$  and  $p_z$  symmetries, respectively.