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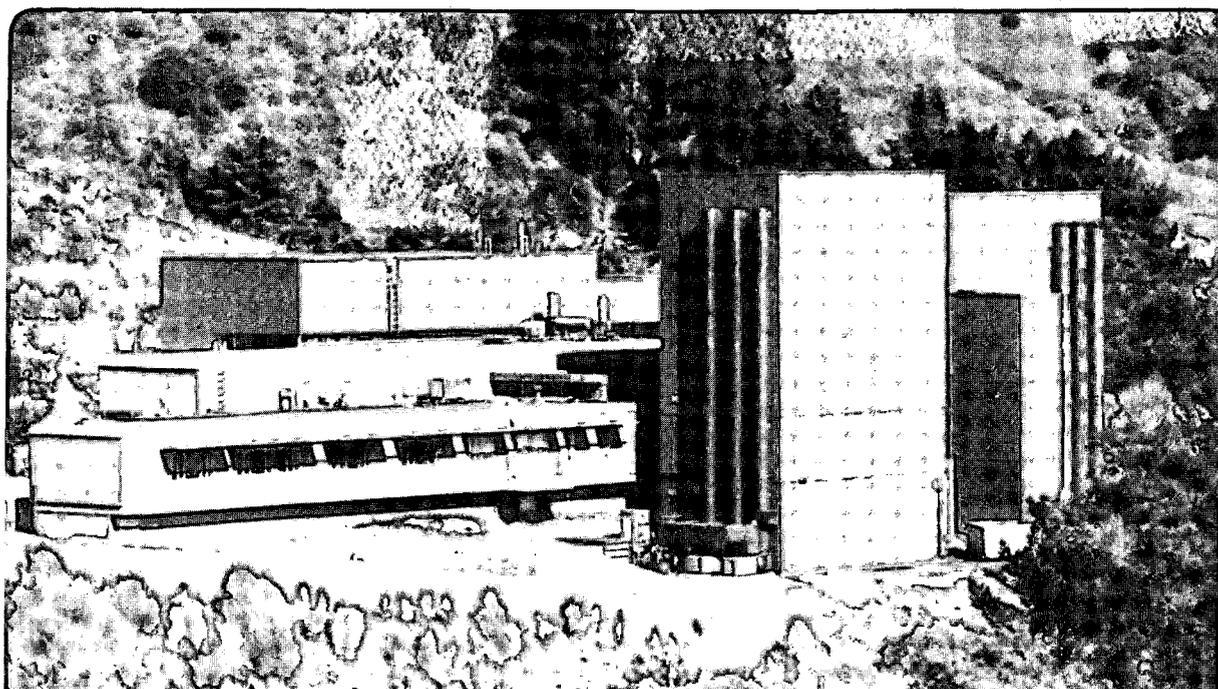
K.M. Krishnan

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Structure of newly synthesized BC₃ films

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Abstract

We have measured the electron energy-loss spectrum of BC₃ at sub-eV resolution. Important differences between the total density of states of BC₃ and graphite at the threshold of the K edge, predicted by earlier *ab initio* calculations, have been observed. We conclude from our measurements that the atomic arrangement in these materials can be described as graphitic sheets with B replacing every third C atom. We suggest that further understanding of the electronic structure of BC₃ can be derived by comparing such EELS data with calculations of the local density of states of bulk BC₃ and including inter-layer interactions.

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A novel graphite material, BC₃, has been synthesized by the interaction of benzene and boron trichloride at 800 °C [1]. These reactions: $2 \text{BCl}_3 + \text{C}_6\text{H}_6 \rightarrow 2 \text{BC}_3 + 6 \text{HCl}$, are driven by favourable TDS values associated with HCl elimination. The films can be deposited coherently on a variety of substrates, and under slow growth conditions, have a preferred orientation with sheet-like character and a metallic appearance. Characterization of these materials by a variety of methods [1,2] have shown them to be graphite hybrids and based on the observed symmetries an ordered structure has been suggested [1]. This is reproduced in figure 1. However, apart from the synthesis and some preliminary electron energy-loss spectroscopy (EELS) measurements there is very little direct evidence to confirm the proposed structure.

Calculations of the electronic structure of this material using the pseudo-potential approach have shown that even though a monolayer of BC₃ is found to be a semiconductor, interlayer interactions could account for their bulk metallic behaviour [3]. Further, for a BC₃ monolayer it was shown that the Fermi level (E_F) was at the top of the σ band and that semimetallic behaviour is due to the presence of σ and π bands at E_F . More recently, important differences in the density of states (DOS) of BC₃ from graphite, derived from the structure proposed in figure 1 has been predicted [4]. Two sharp peaks in the DOS associated with the π band below the conducting σ bands, unlike graphite with one peak, are observed. Observation of this feature should provide direct evidence for the atomic arrangement in this material as the former is a direct consequence of the proposed structure. In this letter, we present transmission electron energy-loss spectroscopy data at high energy resolution of BC₃ and discuss these results in light of the above electronic structure calculations.

All electron energy-loss spectra were recorded at 120kV using a JEOL 200CX transmission electron microscope and a Gatan 666 parallel-detection spectrometer. The

instrument was optimized for high energy resolution ($\sim 0.6\text{eV}$) by substantially cutting down the emission of the source. This resulted in a loss of signal intensity and consequently, an increase in the statistical noise of the data was observed. The samples were prepared by crushing them in a mortar and pestle and then floating them on holey carbon grids. Electron transparent regions of the sample were observed in image mode (diffraction coupling) with an energy dispersion of 0.1eV per channel, a beam divergence of 3.5 mrad s and a spectrometer entrance aperture subtending an angle of 6.8 mrad s. All spectra were normalized with respect to a channel to channel gain variation spectrum to minimize any variation due to the difference in the detection efficiency of the individual elements of the diode array. A standard power law, AE^{-T} , was used to model the background for quantification. Peak positions were calibrated using a highly oriented pyrolytic graphite (HOPG) standard and assuming the peak of the sharp $1s-\pi^*$ transition to be at 285 eV . In general, there are instrumental difficulties in measuring absolute energy positions in transmission EELS experiments. However, the relative values are accurate to $\sim 0.5\text{eV}$.

Representative K-edge spectra of B and C obtained from a thin foil of BC_3 are shown in figure 2. This data can be used to confirm that the stoichiometry of the new material is indeed BC_3 prior to a detailed interpretation of the fine structure in the electron energy-loss spectrum. The quantification procedure is straightforward [5] and requires only a measurement of the integrated intensity, after background subtraction, over a particular energy window above the onset of the edge. The ionization cross-sections used for microanalysis were based on hydrogen-like wavefunctions with appropriate scaling to account for the nuclear charge and screening effects [5]. The results are shown in Table I and confirm that B to C ratio in these films is 1:3.

Based on the electronic structure calculations [3,4], the major difference between the DOS of graphite and BC_3 (for the proposed structural model) appear in the π bands.

The discussion of the EELS data is therefore restricted to the interpretation of the features at the threshold, i.e. $1s-\pi^*$ transitions observed in this material. Higher energy-loss features corresponding to $1s-\sigma^*$ transitions, observed both in the B-K edge (199eV) and in the C-K edge (295eV) are not pertinent to the discussion here and will be addressed separately.

The fine structure of the B K-edge (figure 2) shows two sharp peaks at 187.5eV and 190.1eV. These peaks can be assigned to the excitation of the $1s$ electrons to unoccupied levels in the conduction band. For the ordered structure shown in figure 1, the total DOS of a BC_3 monolayer as calculated in [4] and reproduced in figure 3, indicate that E_F lies at the top of the σ band. This is unlike graphite where E_F lies in the middle of the π band. Further, the π bands are split into two peaks (marked by arrows in figure 3) separated by ~ 3.0 eV. This splitting is attributed to the lowering in translational symmetry caused by the ordered presence of B in the structure [4]. Even though, the accuracy of the position in energy of the conduction band eigenvalues is limited in such calculations, it seems reasonable to assign these splittings predicted by the calculations to the two near-edge peaks separated by 2.6eV observed in the EEL spectrum. However, the same calculations [4] suggest that even though the splitting of the π band is evident in the partial contributions of both the B and C orbitals to the total DOS, the major contribution is from the C local DOS. This is not borne out by the EELS experiments. The C K-edge (figure 2) shows only a single π^* feature at 285 eV and its splitting is not observed even at sub eV resolution. In an earlier calculation by the same group [3], the total DOS of bulk BC_3 shows significant difference between two stacking sequences of the structure shown in figure 1. The BC stacking model, in which the sheets are arranged such that both neighbours, above and below, for the B atoms are C atoms (and vice versa for C atoms) shows a distinct splitting in the π region of the conduction band in agreement with our experimental observation. For the BB stacking, the same peaks are far less pronounced [3]. In addition, this also points out the importance of interlayer interactions in both *ab*

initio calculations of the total DOS and the interpretation of transmission EELS measurements of BC₃.

In summary, these high resolution EELS data support the proposed structure (figure 1) for the BC₃ graphite compound. The predicted total DOS for a BC stacking, i.e. B on C, as opposed to a BB stacking, i.e. B on B, is in agreement with experiment. However, since the initial core-level sites are highly localized it is more appropriate to interpret such fine structures observed in EELS measurements in terms of the local density of states evaluated at a particular site [5]. Additional calculations of the electronic structure of BC₃, with emphasis on the local DOS and including interlayer interactions will be essential to make any progress in the understanding of the structure of these materials using fine structure EELS measurements.

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References

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Table I

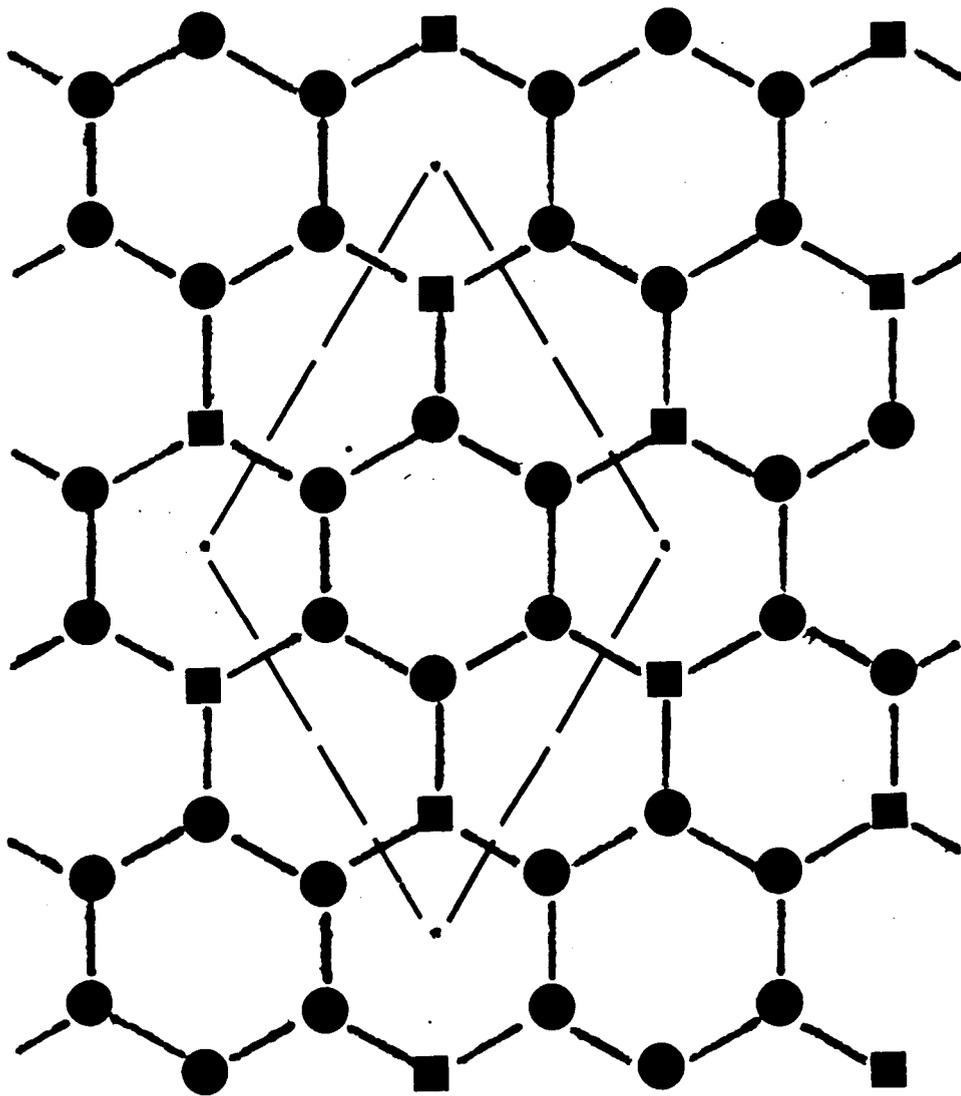
Element	Energy Window (eV)	Integrated Intensity Counts	Cross-Section 10^{-20}cm^2	Atomic Percent
Boron	187-247	848165	0.66	26.02 ± 2.0
Carbon	282-342	2751954	0.25	73.98 ± 4.0

Figure Captions

[1] Proposed structure for the BC₃ graphite material. This atomic arrangement of a single layer was originally suggested in Ref 1. Two stacking sequences of these layers are possible: BB, where the nearest neighbours, both above and below are the same and BC where they are different. The unit cell is indicated by dashed lines.

[2] Electron energy-loss spectra of Boron and Carbon from a thin (~30 nm) sample of BC₃. Only the K edges are shown. A C-K edge trace for graphite (dotted) at 1.0 eV resolution is also superimposed for comparison. Note that the energy scale corresponds to the B-K edge and the C-K edges are plotted such that their respective onsets are superimposed.

[3] Total DOS of a BC₃ (a) and graphite (b) monolayer as calculated in Ref. 4.



● C

■ B

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Fig. 1

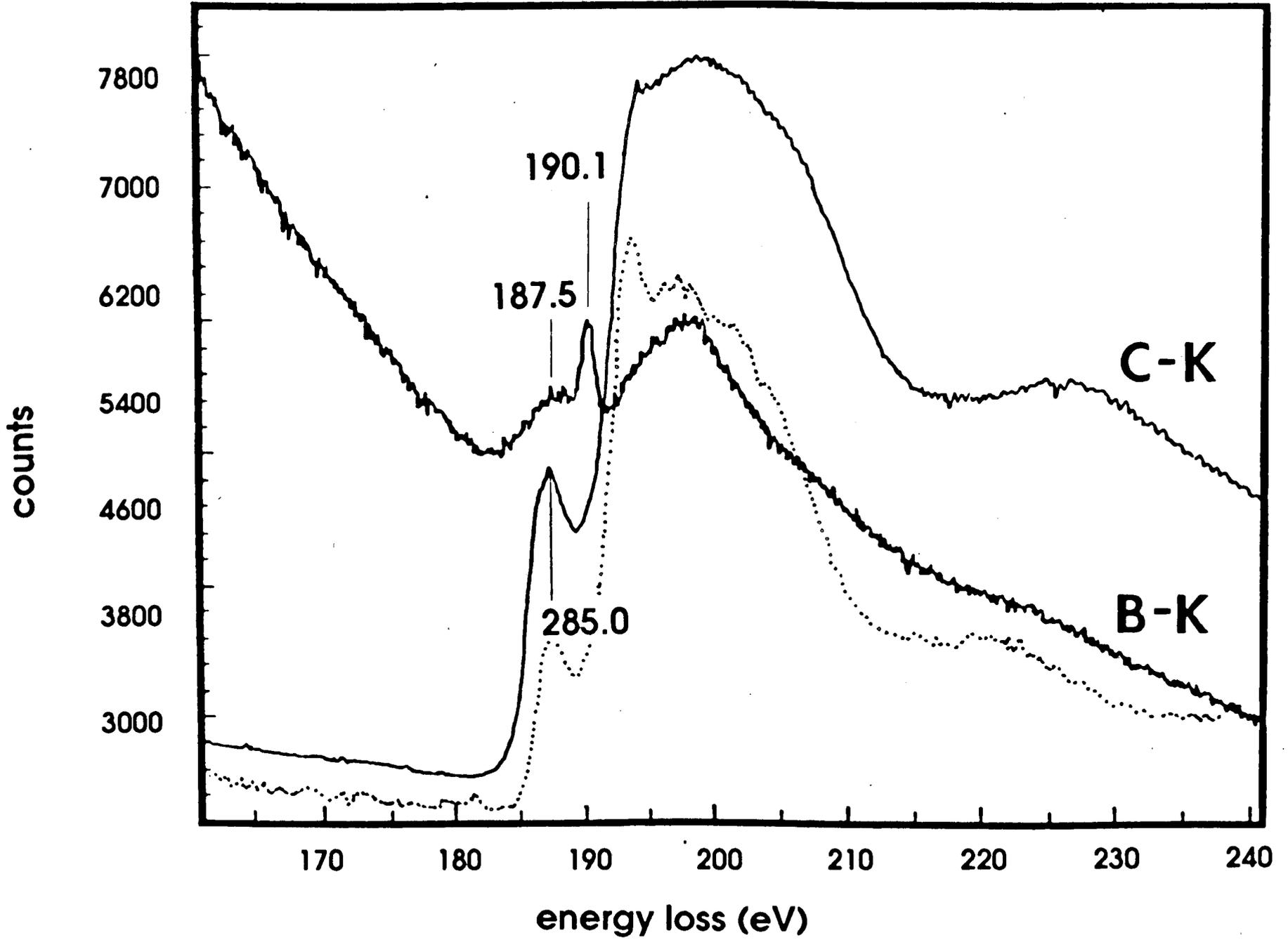
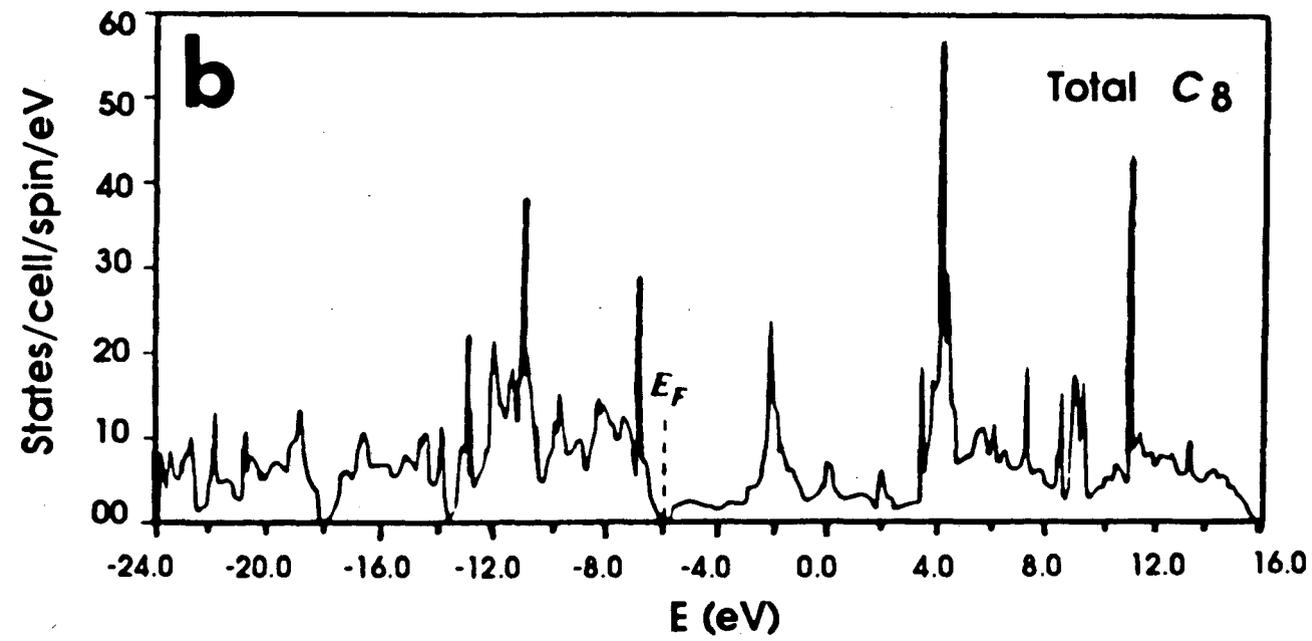
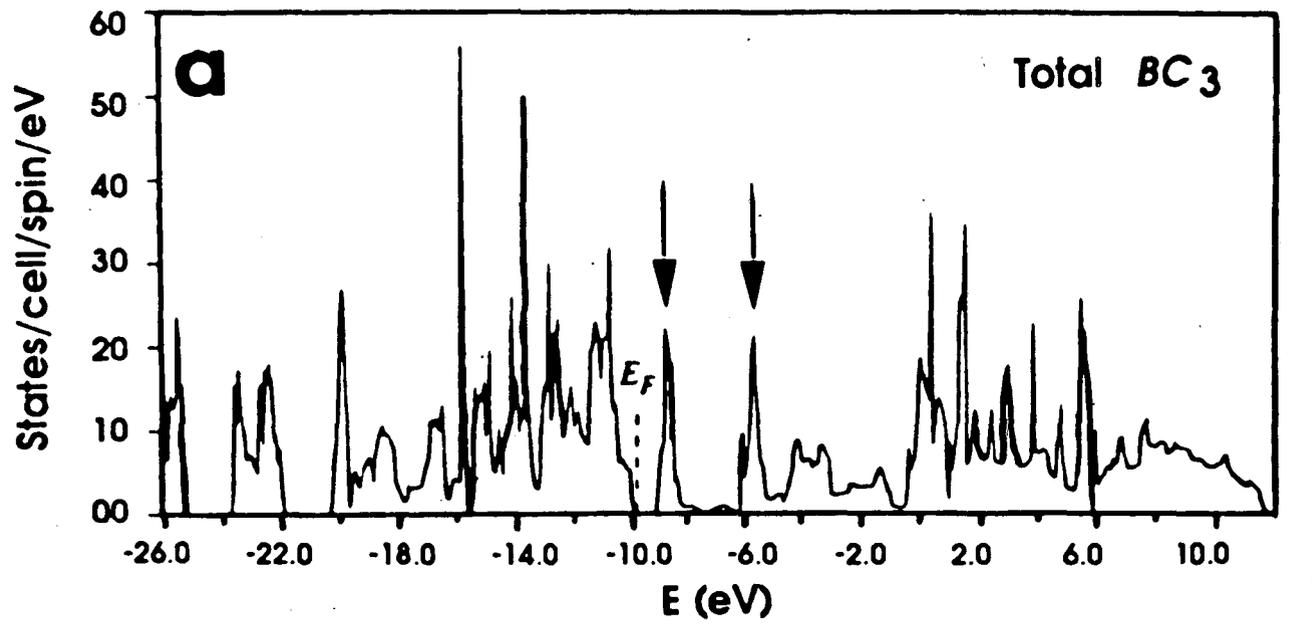


Fig. 2

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Fig. 3

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