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Yoshiteru Takagi [a] & Koichi Kusakabe [a]

[a] Graduate School of Science and Technology, Niigata University, Ikarashi, 950-2181, Japan

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FIRST PRINCIPLES STUDY OF ELECTRONIC STRUCTURES OF DIRECT BAND GAP SEMICONDUCTORS, GRAPHITE FLUORIDES

Yoshiteru Takagi and Koichi Kusakabe
Graduate School of Science and Technology,
Niigata University, Ikarashi 950-2181, Japan

By the first-principles calculation, we show that graphite fluorides have a potential for application as optical devices with near ultraviolet light emission.

Keywords: a first-principles calculation; graphite fluoride; direct gap semiconductor; optical devices

Graphite fluorides CF and C_2F are known to be optically transparent insulators [1]. Since they have a large direct band gap [2,3], they are expected to be utilized as basic materials for optical devices. In order to evaluate the potential of graphite fluorides, we investigated electronic structures of CF and C_2F and determined optical transition matrices.

In our calculation, we used the Troullier-Martins pseudopotential and the plane-wave basis sets to expand valence wave functions. The cut off energy was 150 Ry. Actual calculations were done using the FHI package [4].

Graphite fluorides CF and C_2F are graphite intercalation compounds with strong bonds between intercalants and the graphite sheet. Illustrations of their structures are shown in Figures 1(a) and (b). CF and C_2F belong to the point group D_{3h}. In our calculation, integration over the Brillouin zone (BZ) was carried out using 12 k-points reduced by symmetry of the lattice.

Band structures of optimized CF and C_2F are shown in Figures 1 (c) and (d). The optimized lattice constants are presented in Ref. 3. The valence

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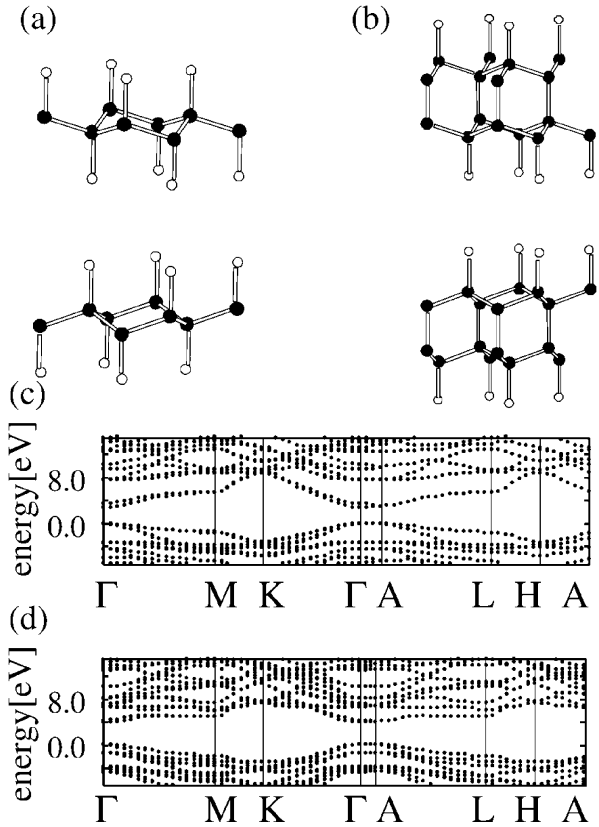

FIGURE 1 Structure of CF (a) and of C_2F (b). White and black circles represent carbon atom and fluorine atoms, respectively. Band structures of the optimized CF (d) and C_2F (c) around the band-gap are also shown.

band top is set at the zero energy in Figure 1. The band structures show that CF and C_2F have a direct band gap at Γ-point in the 1st BZ. Values of the band gap are 2.74 eV and 3.82 eV for CF and C_2F, respectively.

Rescaling of the band gap is required to estimate the band gap in real materials from the LDA calculation, because LDA underestimates the band gap in general. We have estimated the band gap of CF and C_2F by multiplying a factor between the calculation and the observed value for the diamond. The estimation gave the band gap of $\sim$3.8 eV and $\sim$5.4 eV for CF and C_2F, respectively. The band gap are within a near ultraviolet region, when the values are converted into the wave length of light. This estimation is consistent with an experimental fact that CF and C_2F are optically transparent insulators.

TABLE 1 Optical Gaps and OTM Elements in CF and C_2F. OTM_i Represents the ith ($i = x, y, z$) Component of OTM. ○ or × Represent that Dipole Transition is Allowed or is not Allowed Between the States, Respectively. Optical Gap Values Between the Two States are Shown in the Second Column for CF and the Third Column for C_2F in eV

Transition	CF	C_2F	OTM_x	OTM_y	OTM_z
Γ_1^{VB}–Γ_1^{CB}	2.74	3.82	×	×	×
Γ_1^{VB}–Γ_2^{CB}	3.41	4.29	○	○	×
Γ_2^{VB}–Γ_1^{CB}	2.88	3.84	○	○	×
Γ_2^{VB}–Γ_2^{CB}	3.44	4.31	×	×	×

As mentioned above, CF and C_2F are direct band gap semiconductors with a wide band gap. To confirm that it is possible to utilize CF and C_2F as optical devices, we next evaluated the values of the optical transition matrix (OTM). Obtained elements of OTM are summarized for CF and C_2F in Table 1. Here, Γ_1^{CB} and Γ_2^{CB} are the lowest conduction state and the second lowest conduction state at Γ-point. Similarly, Γ_1^{VB} and Γ_2^{VB} are the highest valence state and the second highest valence state at Γ-point. (See Fig. 2.) OTM elements between Γ_1^{CB} and Γ_1^{VB} are zero. However, OTM elements between Γ_2^{VB} and Γ_1^{CB} are finite. The energy difference between Γ_1^{VB} and Γ_2^{VB} is about 40 meV for CF and it is about 20 meV for C_2F. Therefore, two levels are almost equally filled with electrons at room

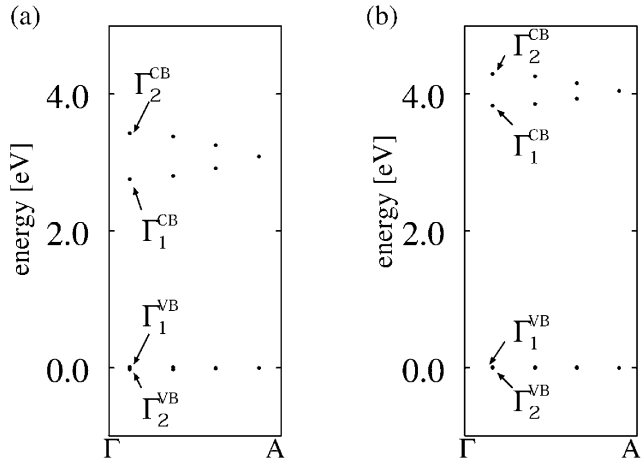

FIGURE 2 Band structure of the optimized CF (a) and C_2F (b) around the band-gap on the Γ-*A* line. In the figures, band indices are indicated.

temperature. As a results, it is expected that CF or C_2F act as optical devices at room temperature.

In this paper, we showed that graphite fluorides are useful for optical devices with near ultraviolet light emission. In addition, we have reported in a separate paper that the band gap changes from a direct one to an indirect gap by changing stoichiometry of C_nF compounds [3]. Here, the lattice structure of C_nF ($n > 2$) is assumed to be a stacking of C_nF sheet made by sp^3 bondings similar to CF or C_2F. We have shown that C_nF ($n > 3$) has an indirect band gap similar to that of diamond. If we can construct a structure like, . . ./C_nF/CF/C_nF/. . ., the structure should become a superlattice of direct gap semiconductors and indirect gap ones. Fabrication of C_nF films on a diamond surface covered by F, if possible, should be a basic strategy to create optical devices. Moreover, there are many candidates to doping electrons or holes into CF and C_2F. The doping may be achieved by chemical doping, e.g. fluorination of BC_xN compounds, intercalation, and field effect [5].

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