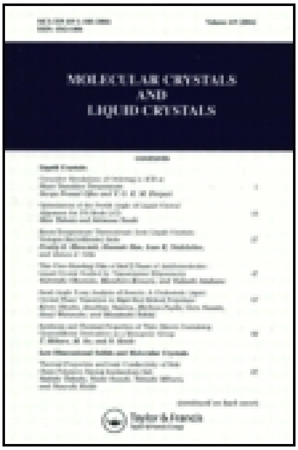

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Theoretical Study on Structure and Electronic State of Sodium-Hydrogen-Graphite Ternary Intercalation Compound

Shinichi Higai [a] [d] , Toyoki Fujiwara [a] , Shugo Suzuki [a] , Seiji Mizuno [b] [c] & Kenji Nakao [a]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, 305-8573, Japan

[b] Institut für Theoretische Physik, Technische Universität Dresden, D-01062, Dresden, Germany

[c] Department of Applied Physics, Hokkaido University, Sapporo, 060-8628, Japan

[d] National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, 305-0047, Japan

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Theoretical Study on Structure and Electronic State of Sodium-Hydrogen-Graphite Ternary Intercalation Compound

SHIN'ICHI HIGAI[a*], TOYOKI FUJIWARA[a], SHUGO SUZUKI[a],
SEIJI MIZUNO[bc] and KENJI NAKAO[a]

[a]*Institute of Materials Science, University of Tsukuba, Tsukuba 305–8573, Japan,* [b]*Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany and* [c]*Department of Applied Physics, Hokkaido University, Sapporo 060–8628, Japan*

We have theoretically studied the structure and electronic state of the sodium-hydrogen-graphite ternary intercalation compound based on the first-principles calculation. As concerns the structure, it is suggested that intercalated hydrogen is in the H_2 molecular form. As for the electronic state, both the antibonding π^*-bands of graphite and $1s\sigma^*$ band of H_2 with a small dispersion form the metallic states.

Keywords: graphite intercalation compound; sodium; hydrogen; structure; electronic state; electric field gradient

INTRODUCTION

Among the alkali metals, sodium shows a peculiar behavior to graphite, i.e., it hardly forms the graphite intercalation compound (GIC). Interestingly, it forms the ternary GIC with hydrogen similarly to the other alkali metals[1]. Up to the present, the structure and electronic state of the sodium-hydrogen-(Na-H-)GIC have not been established yet. As concerns the structure, the point which attracts much interest is how intercalated H exists in this compound. Moreover, as for the electronic state, what character of the energy band forms the metallic state and contributes to the electric conduction. In the present work, we have performed the first-principles cal-

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* Present address: National Research Institute for Metals, 1–2–1 Sengen, Tsukuba, 305–0047, Japan

culation in order to reveal them. Furthermore, to determine the form of H, we have calculated the nuclear quadrupole coupling constant and asymmetry parameter for Na, and compared them with those obtained from the ^{23}Na nuclear magnetic resonance (NMR) measurement for Na-H-GIC[2].

STRUCTURAL MODELS

We have constructed simple structural models for Na-H-GIC based on the experimental results[2–4]. Here we explain these models, which are presented in Fig. 1. Their chemical formula has been settled to be $C_{4s}NaH$ (s: stage number). Intercalated Na and H form separate Na-H-Na triple layers. The distance between the graphite layers which sandwich them is 7.23 Å. In the Na layer, Na forms the (2×2) triangular lattice structure. The arrangement of H has not been clarified, so that we had to assume it. We have made up eight models for candidates, which are noted as *A-a*, *A-x*, *A-y*, *A-z*, *B-a*, *B-x*, *B-y*, and *B-z*. The first letters *A* and *B* denote the sites where H places. As shown in Fig. 1, the *A* and *B* sites are the center of the graphite hexagon and middle of the C-C bond, respectively. Two kinds of forms can be considered for intercalated H, i.e., the isolated H atom and H_2 molecule. The models in which H exists as a H atom (H models) are denoted by the last letter *a*. On the other hand, the models in which H exists as a H_2 molecule (H_2 models) are denoted by x, y, and z, each of which indicates the direction of the H_2 molecular axis. In these models, the z axis is chosen as parallel to the c axis. For the H_2 models, the bond length of H_2 is optimized.

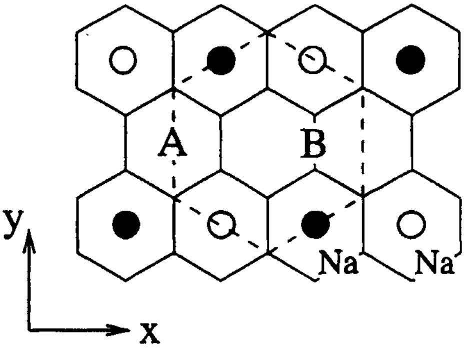

FIGURE 1 The top view of the structural model for Na-H-GIC. Graphite is presented by the hexagonal net. The Na atoms are given by open and closed circles. The H atoms are placed on the *A* or *B* site. Dashed lines indicate a unit cell. The stacking order along the c-axis direction is -C-Na(○)-H-Na(●)-C-.

RESULTS AND DISCUSSION

In the present calculation, we have adopted the full-potential linear combination of atomic orbitals method using the numerical multiple basis set[5], based on the local density functional formalism[6].

For the first step, in order to determine the form of H in this compound, we have carried out the calculation for the above models. In Table I, we give the obtained values of the cohesive energy E_{coh}, and the nuclear quadrupole coupling constant e^2Qq_{zz}/h (e: elementary electric charge, Q: quadrupole moment, q_{zz}: maximum eigenvalue of the electric field gradient, h: Planck constant), asymmetry parameter η, and direction of the principle axis for the minimum eigenvalue q_{xx} for Na, for each model.

Firstly, it is found from E_{coh} that the H models, *A-a* and *B-a*, are energetically less stable than the H_2 models. In addition, one of the H_2 models, *A-z*, is also unstable. Among them, the most stable model is *A-y*.

Secondly, let us compare e^2Qq_{zz}/h and η with those obtained from ^{23}Na-NMR[2], which are also presented in Table I. Two sets of these values have been derived depending on the choice of the q_{xx} direction. When q_{xx} is chosen as parallel to the *c* axis, e^2Qq_{zz}/h and η are 1.80 MHz and 0.85, respectively. On the other hand, when q_{xx} is in the *ab* plain, they are 1.69

TABLE I The cohesive energy E_{coh} with the difference Δ to the largest value, and the nuclear quadrupole coupling constant e^2Qq_{zz}/h, asymmetry parameter η, and direction of the principle axis for the minimum eigenvalue q_{xx} for Na, calculated for each structural model, and the experimental value.

Model	E_{coh} [eV/atom]	Δ	e^2Qq_{zz}/h [MHz]	η	q_{xx}
Stage-1					
A-a	6.484	−0.054	−2.21	0.06	*c*
A-x	6.529	−0.009	1.31	0.04	*c*
A-y	6.538	0.0	−1.47	0.79	*ab*
A-z	6.485	−0.053	−1.31	0.86	*ab*
B-a	6.481	−0.057	−3.03	0.47	*c*
B-x	6.535	−0.003	−0.75	0.45	*ab*
B-y	6.531	−0.007	−1.83	0.17	*ab*
B-z	6.523	−0.015	−1.46	0.20	*ab*
Stage-4					
A-y			−1.57	0.80	*ab*
Error	±0.01		±0.2	±0.3	
Experiment			1.80	0.85	*c*
			1.69	1.00	*ab*

MHz and 1.00, respectively. In either case, these values show that the eigenvalue ellipsoid of e^2Qq/h has a unique shape, i.e., a quite squashed shape. For the H models, e^2Qq_{zz}/h are much larger than the experimental values, while η are much smaller. On the other hand, for the H_2 models, e^2Qq_{zz}/h are very close to the experimental values, except *B-x*. However, as for η, only *A-y* and *A-z* are desirable. Taking E_{coh}, e^2Qq_{zz}/h, and η into account, it is concluded that only the *A-y* model is the appropriate one. Accordingly, it is suggested that the intercalated H is in the H_2 molecular form.

The above calculation has been done for the stage-1 models. Though, ^{23}Na-NMR has been measured for the stage-4 compound, which is the minimum stage number succeeded in the isolation. Then, we have also done the calculation for the stage-4 *A-y* model. The obtained e^2Qq_{zz}/h and η are given in Table I. Differences between the values for the stage-4 and -1 models are very small. Thus it is concluded that the stage number scarcely affects them.

Concerning the form of H in Na-H-GIC, there is another possibility that H is in the NaH molecular form. However, this is also denied by the following reason. If H forms the NaH molecule, the Na-H interatomic distance becomes smaller than those in the H models. As a consequence, e^2Qq_{zz}/h also becomes much larger.

For the Na-H-C_{60} solid, which is the ternary system also made up of Na, H, and C, both the calculational and experimental values of e^2Qq_{zz}/h and η for Na have been obtained, too[7,8]. The former are −3.3∼−3.2 MHz and 0.47∼0.57 for the assumed structural model with the chemical formula Na_4HC_{60}, and the latter are 3.7 MHz and 0.95. It has also understood that H in this compound exists in the atomic form. Comparing with e^2Qq_{zz}/h for Na-H-GIC, that for Na-H-C_{60} is much larger. Hence it is most likely that the difference in e^2Qq_{zz}/h reflects the difference in the form of H.

For the next step, we have calculated the electronic band structure for the most plausible model *A-y* (stage-1), and the result is shown in Fig. 2. The overall band structure is understood as the superposition of the Na 3*s*- and H 1*s*-bands on the bonding π- and antibonding π^*-bands of graphite, which linearly degenerate at −6.2 eV. Two Na 3*s*-bands exist above the Fermi level (E_F), in the region higher than −4.5 eV. On the other hand, reflecting the H_2 molecular form, two H 1*s*-bands are widely split. We see the band with little dispersion at −12.5 eV, which is originated in the 1*sσ* state. While the band originated in the 1$s\sigma^*$ state exists near E_F (−5.8∼−4.5 eV), in which the Na 3*s*-state is considerably hybridized. The most noticeable feature of this band structure is the participation of two different

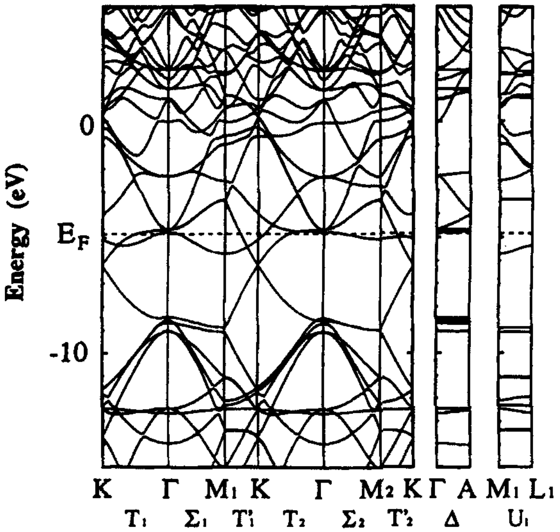

FIGURE 2 The electronic band structure for the structural model A-y (stage-1). The dashed line indicates the Fermi level.

types of bands in the conduction state, which are the graphite π^*- and H_2 $1s\sigma^*$-bands. They intersects E_F, and form the electron and hole Fermi surfaces, respectively. However, the mobility of the hole carrier may be much smaller than that of the electron carrier, due to the small dispersion of the $1s\sigma^*$ band and the defects in the intercalate layers.

The charge transfer (CT) from the intercalates generates the electron carrier in the graphite π^*-band, as in the usual donor type GIC. We have estimated the amount of CT per a Na-H unit for the A-y (stage-1) model, which has been obtained as 0.14. For a comparison, we have converted the amount of CT estimated per a C atom from ^{13}C-NMR (stage-4)[3] and the Shubnikov-de Haas oscillation (stage-5)[9] into the above unit, which have been obtained as 0.27 and 0.19, respectively. These values are a little larger than ours, but the differences are not large.

In discussing the electronic states of GIC's, the behavior of the interlayer state has attracted considerable interests. In our calculation, the unoccupied atomic orbitals have also been used for the basis set, and thus we can investigate it. In the band structure of Na-H-GIC, the character of the interlayer state is hybridized into the Na 3s-bands above E_F, though it is hardly seen in the occupied states.

We have suggested the form of intercalated H as the H_2 molecule. In addition, we have also estimated the frequency of the H_2 molecular oscillation with the harmonic approximation. The bond length of H_2 extends from 0.74 Å for an isolated molecule to 0.84 Å, because of CT from the Na $3s$-state to the H_2 $1s\sigma^*$-state. Therefore, the obtained value 2090 cm^{-1} is much downshifted from 4401 cm^{-1} for an isolated one. If the frequency close to it would be observed for Na-H-GIC by the Raman spectroscopy, our suggestion would be supported.

CONCLUSION

In the present work, the structure and electronic state of Na-H-GIC have been investigated from the theoretical aspect. On the basis of the energetics and electric field gradient for Na, it has been suggested that intercalated H prefers the H_2 molecular form rather than the isolated atomic form. In the electronic state, the graphite π^*-bands form the metallic states together with the H_2 $1s\sigma^*$-band with a small dispersion. Consequently, Na-H-GIC has been classified into the donor type.

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