



Amorphous BC₅ from first principles calculations

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ABSTRACT

A boron-substituted amorphous graphite (BC₅) network is generated using a first principles molecular dynamics simulation and its atomic structure and electrical and mechanical properties are discussed in details. The network has a layered structure with primarily hexagonal (six membered) rings and its average coordination is about 3.0. The material is a solid solution having a minor amount of B-B homopolar bonds. It is structurally different from the BC₅ crystal or monolayers proposed in the literature. The model is a semimetal material based on a generalized gradient approximation with the Hubbard correction (GGA+U) calculation. When its mechanical properties are concerned, they are comparable with those of graphite or amorphous graphite.

1. Introduction

Graphite is one of most extensively studied materials and has various high-tech applications. Its properties can be easily altered by chemical doping [1–5], chemical functionalization [6–8] etc. The incorporation of boron (B) into graphite appears to be an effective way to change its properties [1–5,9,10]. Various graphite-like B-C phases with different stoichiometry up to 50 at.%, so called *B-substituted graphites*, have been fabricated by thermal chemical vapor deposition (CVD) technique [4]. These materials have been attracted considerable attention because they can serve as perfect precursors to synthesize superhard diamond-like B-C phases [11]. However, the properties of B-substituted graphites at neither ambient and nor high temperature and pressure conditions are still not established yet.

Amongst B-C phases, BC₅ is particular interest because its diamond-like structure shows superior properties such as a large bulk modulus, high fracture toughness, high hardness, high thermal stability and superconductivity [11,12]. The formation of a graphite-like BC₅ material was first proposed by Way et al. [13]. In the same study, it was suggested that B atoms form an ordered arrangement within each layer. Another experiment reported a single phase of BC₅ having a well-defined two-dimensional (2D) structure and its metallic nature [14]. However, how B atoms are distributed in the BC₅ monolayer and how the BC₅ layers are stacked up to form a crystalline structure are still not clear. Earlier studies proposed isolated and homogeneously distributed B atoms for the monolayer and crystalline phases [15,16]. Later, however, a theoretical investigation based on the particle swarm optimization method offered that the most stable 2D structure of BC₅ consisted of

one-dimensional (1D) zigzag B chains [17]. Indeed, ¹¹B-NMR measurements revealed the formation of B-B bonds at high B content materials, for example, B_{0.13}C_{0.87} [4]. Consequently, the existence of B-B bonds can be anticipated for the BC₅ structures but in what form is still unknown.

B doped amorphous graphite (a-graphite) up to 25 at.% was prepared using a high-temperature pyrolysis assisted CVD method [18]. From this experiment, it can be inferred the presence of amorphous BC₅ (a-BC₅). However, the atomic structure, specifically B distribution, and the mechanical properties of B substituted a-graphites have not been explored yet. Understanding the properties of a-BC₅ is indeed particularly important because it can serve as a precursor to produce an amorphous diamond-like phase that might possess some superior properties like *amorphous diamond*. In this study, we use ab initio calculations to reveal, for the first time, the properties of a-BC₅ and compare them with those of graphite and a-graphite.

2. Computational method

The amorphous model was prepared using the SIESTA ab initio package [19] with a pseudopotential approach [20]. The exchange correlation term was computed using a generalized gradient approximation (GGA) [21,22]. The forces and total energies were computed at the Γ point. Double- ζ basis sets were chosen for the calculations. Molecular dynamics (MD) simulations with 1.0 fs for each time step were executed within the isothermal–isobaric ensemble (NPT) and we chose the velocity scaling (temperature) and the Parrinello-Rahman technique (pressure). We selected a 216 atoms BC₃ melt as a starting structure and

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created a BC₅ configuration by replacing some B atoms with C atoms. The BC₃ melt at 4000K has an average coordination number of 3.11 for B-atoms and 2.67 for C-atoms and the mean B-B, B-C and C-C separations are 1.701 Å, 1.50 Å, 1.34 Å, respectively. The starting arrangement was thermalized at 5000 K for 25.0 ps. Thereafter we reduced the temperature applied to 4000 K within 5.0 ps. At 4000 K, the melt was thermalized again for 20.0 ps. Thereafter, we reduced the temperature applied to 300 K with a quenching rate of 2×10^{13} K/s. The configuration at 300 K was relaxed using the variable-cell conjugate gradient scheme. In order to accurately evaluate the electronic feature of the amorphous configuration generated, we also executed the GGA+U simulation implemented in SIESTA. We used a HES06 functional calculation on a BC₃ monolayer [23] as a reference to set the Hubbard potential U and found that the Hubbard potential U=5.0 eV for C-p and U=2.0 eV for B-p yields a band gap energy of 1.83 eV for a 144 atoms BC₃ monolayer, comparable with 1.81 eV produced by the HES06 functional [23]. For the structural analysis, ISAACS [24] program was used. For the visualization of the structure, VESTA [25] program was used.

3. Results

Fig. 1 shows the ball-stick illustration of the computer-generated a-BC₅ model. The network has a-graphite-like structure in which some B atoms attach some layers, consisting with the experiment in which the inserted B atoms between the graphitic planes was proposed for high B content B-substituted graphites [14]. The amorphous configuration is a solid solution, again similar to the ordered BC₅ [13]. The average layer spacing is about 3.47 Å that is analogous to the experimental value of 3.407 Å [14] in the ordered phase and about 3.41 Å (inferred from Fig. 4 of Ref.5) for B-doped a-graphite [5] while it is significantly larger than 3.0 Å for the crystal projected in the theoretical study [15]. The density of the amorphous configuration is 1.90 g/cm³ that is quite less than the density of about 2.18 g/cm³ in the ordered BC₅ [14]. The less densification is commonly seen in the amorphous form of materials.

In order to have particular information regarding the microstructure of the computer-generated amorphous structure, in the next step, we probe its partial pair correlation functions (PPCFs) and provide them in Fig. 2. The mean C-C and B-C bond distances are positioned at around 1.44 and 1.53 Å, respectively. These values are slightly longer than 1.42 and 1.51 Å proposed for the BC₅ crystal in a theoretical study [16]. A small difference might be related to the different exchange correlation functions (LDA vs GGA) used or to nonuniform structural arrangements in the amorphous model. The B-B pair exhibits large variations that are possibly related to statistical noise due to a low content of B atoms. The shoulder positioned at ~1.76 Å in the B-B correlation indicates the presence of B-B homopolar bonds. The distribution of B atoms in the BC₅ systems are not well-known yet. ¹¹B-NMR measurements argue the formation of B-B bonds in materials with high B concentration [4] and

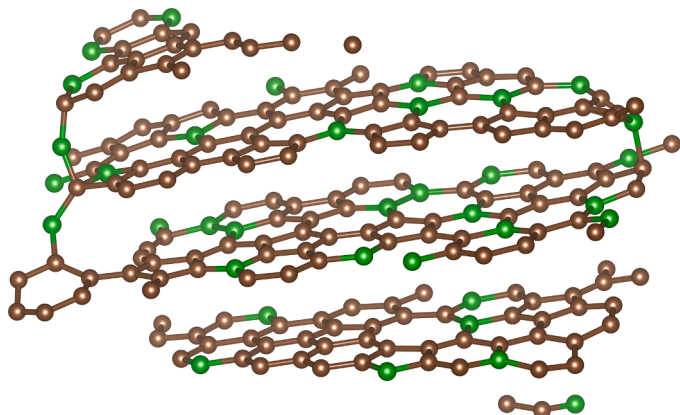


Fig. 1. Visualization of computer-generated a-BC₅ model.

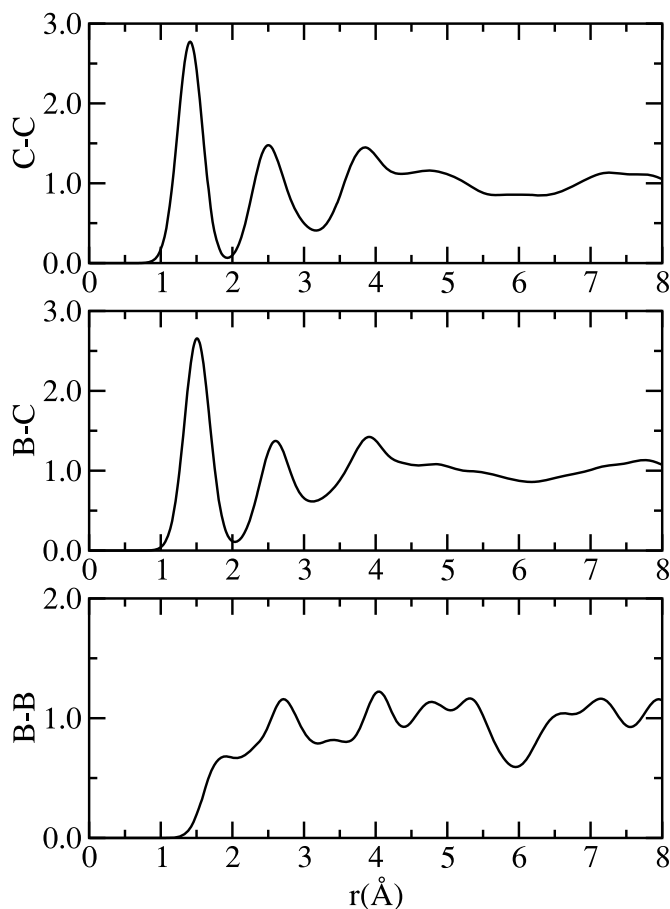


Fig. 2. Partial pair correlation functions (PPCFs) of the a-BC₅ configuration.

hence the development of B-B bonds can be anticipated in a-BC₅ as well but as suggested in a theoretical study for the BC₅ monolayer, 1D zigzag B chains do not form in a-BC₅.

The total and partial coordination numbers are determined using the cutoff radius of B-B= 2.16 Å, B-C= 2.03 Å and C-C= 1.99 Å. Approximately 97 % of C atoms are threefold coordinated and the rest are twofold and fourfold coordinated. The average coordination number of C-atoms is 3.01 and the partial coordination number is 2.45 (C-C) and 0.55 (C-B). On the other hand, roughly 83 % of B atoms are threefold coordinated followed by fourfold coordination (around 11 %). The mean coordination number of B atoms is about 3.05 and the partial coordination number is 2.77 (B-C) and 0.277 (B-B), respectively. The chemical environment analysis given in Table 1 can offer additional knowledge about the local structure. C-C₃ (~ 54%), C-B₁C₂ (~35%), and C-B₂C₁ (~8%) type units are the most common ones around C-atoms. So about 56% C atoms involve at least a bond with B atom. B-C₃ unit (~68 %), signifying isolated B atoms, is the dominant unit around B atoms. B-B₁C₂ (~17 %) is the second primary motif for B atoms.

The atomic structure of the amorphous configuration is further

Table 1
Chemical identities around B and C atoms in the amorphous configuration.

	B	C	
C3	66.67 %	C3	53.89 %
B1C2	16.67 %	B1C2	35.00 %
B1C3	5.56 %	B2C1	7.78 %
C2	5.56 %	B3C1	1.11 %
B2C2	2.78 %	C2	1.11 %
C4	2.78 %	B1C3	0.56 %
		B2C2	0.56 %

analyzed by a three-body correlation function, namely bond angle distribution functions. Some distributions are shown in Fig. 3 and all have a principal peak near 120°, signifying predominant trigonal symmetry. Five-, seven and eight-membered rings, which also exist in a-graphite [26], produce angles near the hexagonal angle. The ring statistical investigation shown in Fig. 4 provides supporting evidence for predominant trigonal symmetry in a-BC₅.

The electron density of states (EDOS) calculated using a GGA+U method is given in Fig. 5. The amorphous structure demonstrates no forbidden gap and the EDOS suggests a semimetallic material. In order to compare the electronic properties of a-BC₅, we constructed an a-graphite configuration by replacing all B atoms with C-atoms in our a-BC₅ model, relaxed it and finally calculated its EDOS. As can be seen from the figure, a-BC₅ and a-graphite networks exhibit quite similar electronic structure and hence we conclude that a-BC₅ is semimetal.

To estimate the bulk modulus of a-BC₅, we probe its energy (E) as a function of volume (V) (see Fig. 6) using a variable cell optimization method and fit the data to the third-order Birch-Murnaghan equation of state

$$E(V) = E_0 + \frac{9V_0K}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 K' + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}$$

The equation of state leads the bulk modulus (K) to be about 33 GP and its pressure derivative (K') to be 4.37. Since there is no information about the mechanical properties of a-BC₅ in the literature, we compare our results with those of graphite and a-graphite (see Table 2) [27–34]. As can be seen from the Table, the K value of a-BC₅ is fairly comparable with 34-38 GPa reported for a-graphite or graphite.

By applying small axial strain (ϵ_{axial}) along the principal axes, we study the stress (σ_{axial})-strain (ϵ_{axial}) relation as shown in Fig. 7. From the slope of the curves, we estimate the average Young's modulus ($E = \sigma_{axial}/\epsilon_{axial}$) to be about 29 GPa, which is practically close to 21-30 GPa projected for the forms of graphite.

From the following two equations,

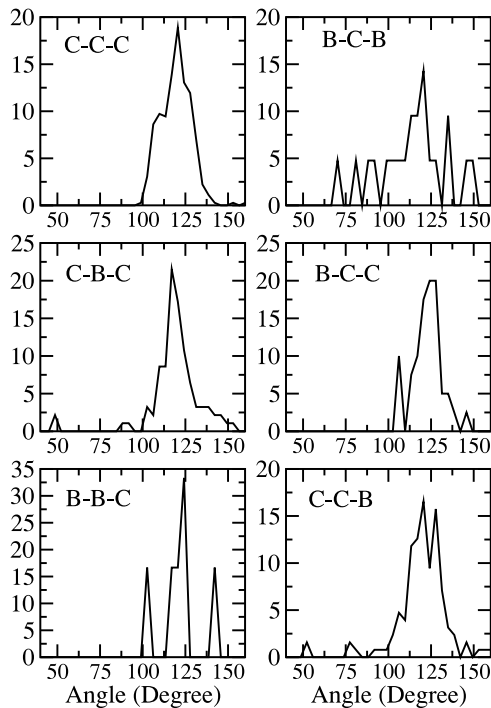


Fig. 3. Bond angle distribution functions of a-BC₅.

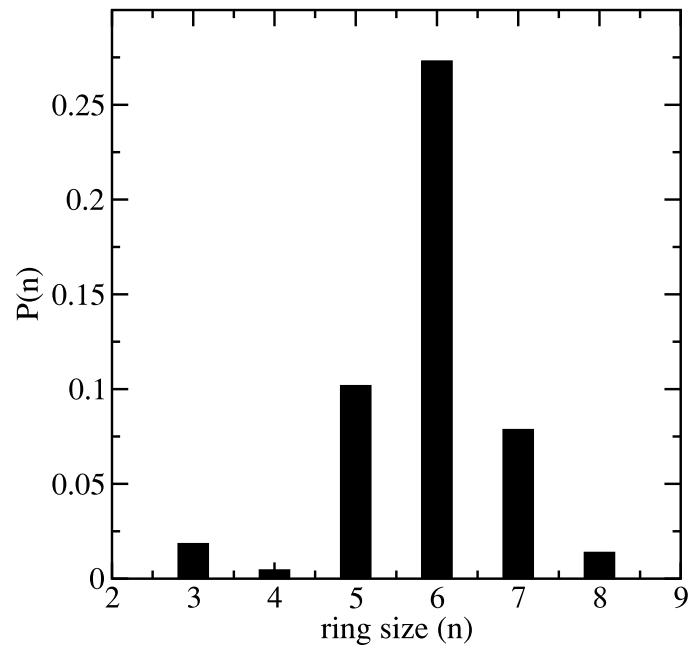


Fig. 4. Ring statistic of a-BC₅.

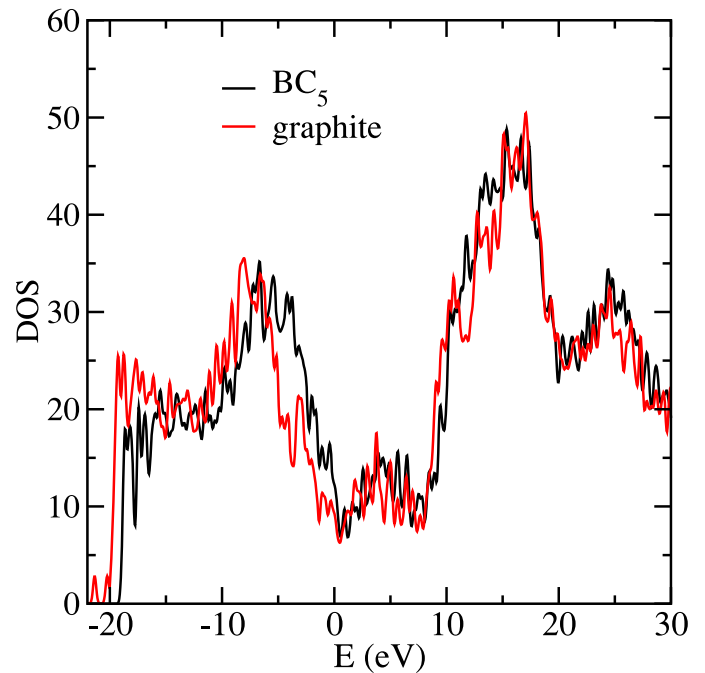


Fig. 5. Electron density of states (EDOS) of a-BC₅ and a-graphite generated by replacing all B atoms with C-atoms in a-BC₅ model.

$$\nu = \frac{1}{2} - \frac{E}{6K} \quad \text{and} \quad \mu = \frac{E}{2(1+\nu)}$$

Poisson ratio (ν) and shear modulus (μ) are calculated to be about 0.35 and 11 GPa, respectively. The shear modulus predicted for a-BC₅ is comparable with that of graphite or a-graphite. On the other hand, the Poisson ratio of a-BC₅ is quite larger than 0.17-0.28 reported for a-graphite but it is sensibly close to that of graphite.

In order to roughly estimate Vickers hardness, we use three different empirical equations $H = 0.151 \mu$ (GPa) [35], $H = 0.92 \left(\frac{1}{n}\right)^{1.137} (\mu)^{0.708}$ (GPa) [36] and $H = 0.0635 E$ [37].

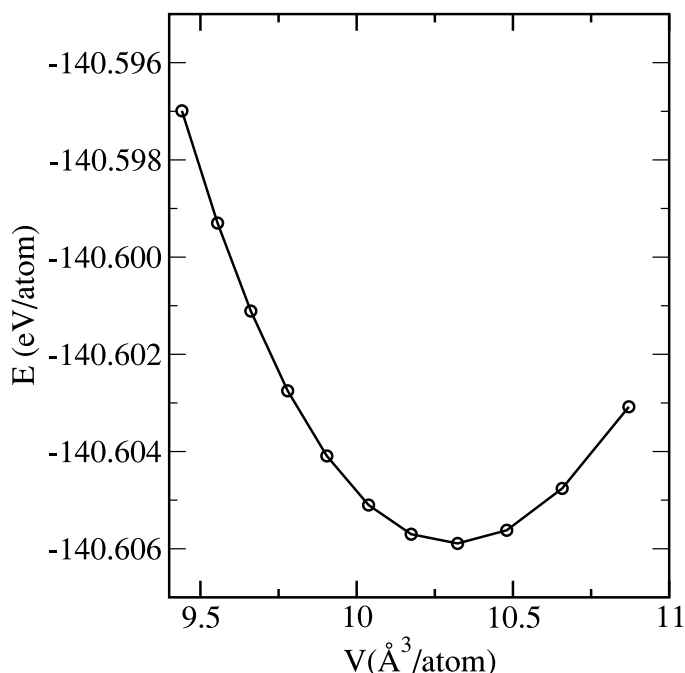


Fig. 6. Variation of energy as a function of volume.

They yield the Vickers hardness is to be 1.63-1.85 GPa, comparable with 1.3-3.0 GPa reported for a-graphite or graphite.

4. Discussion

The structural investigations expose that a-BC₅ has a layered structure with an average layer spacing of 3.47 Å, reasonably close to the experimental value of 3.407 Å [14] in BC₅. Its connectivity, as expected, is parallel to that of a-graphite [26]. Isolated B atoms are dominant but a few B-B bonds do exist in a-BC₅, consisting with the experiment. The local structure of a-BC₅, specifically the distribution of B atoms, appears to be different from that of the crystals or monolayers reported in the literature because B atoms are neither fully isolated and ordered nor form 1D zigzag chains. Considering the number of isolated B atoms and B-B bonds, one might think that a-BC₅ structurally lies between two proposed (crystal or monolayer) structures.

On the basis of GGA+U calculation, we propose that a-BC₅ shows a semimetallic character as in BC₅. Within the accuracy of DFT calculation and the approaches used in present work, we also suggest that a-BC₅ has the mechanical properties, comparable with those of a-graphite. Consequently, considering both electronic structure and mechanical properties of a-BC₅, it shows no superior properties than a-graphite. Yet it should be noted that layer spacing appears to be quite sensitive to reaction temperature [4] and hence depending on preparation techniques and temperatures, a-BC₅ having different properties can be

Table 2

Bulk modulus (K), Young's modulus (E), shear modulus (μ), Vickers hardness (H) and Poisson ratio (ν) of a-BC₅, a-graphite and graphite.

	K (GPa)	E (GPa)	μ (GPa)	ν	H (GPa)	Refs.
a-BC ₅	33.9	29.2	10.8	0.35	1.63-1.85	This study
a-graphite	37.9	28				[27]
		21				[28]
		23-32	10-13	0.28		[29]
				0.12-0.15	2-3	[30]
graphite	33.8	25.5	9.7	0.31		[31]
	36.3	29.8	10.9	0.36	1.3	[32]
						[33]
						[34]

fabricated.

5. Conclusions

We have generated an amorphous BC₅ configuration and exposed its microstructure and mechanical and electronic properties by means of ab initio MD simulations. The amorphous model has a layered structure whose connectivity is mainly hexagonal rings. It is a solid solution having a minor amount of B-B homopolar bonds. It structurally differs from the BC₅ crystals or monolayers proposed in the literature. The model shows a semimetallic nature based on GGA+U simulations. Its mechanical properties are comparable with those of graphite or a-graphite. Our conclusions are interpreted from a 216-atoms amorphous model but they relatively agree with the experimental data and hence we believe that the computer-generated model yields correct information regarding the short-range order of a-BC₅. For larger systems, the number of B-B bonds and fourfold coordination motifs might be different and thus additional accurate simulations on larger structures are compulsory to explore its local structure and properties in details.

CRedit authorship contribution statement

Murat Durandurdu: Investigation, Validation, Formal analysis, Data curation, Writing – original draft, Visualization, Conceptualization, Methodology, Resources, Funding acquisition.

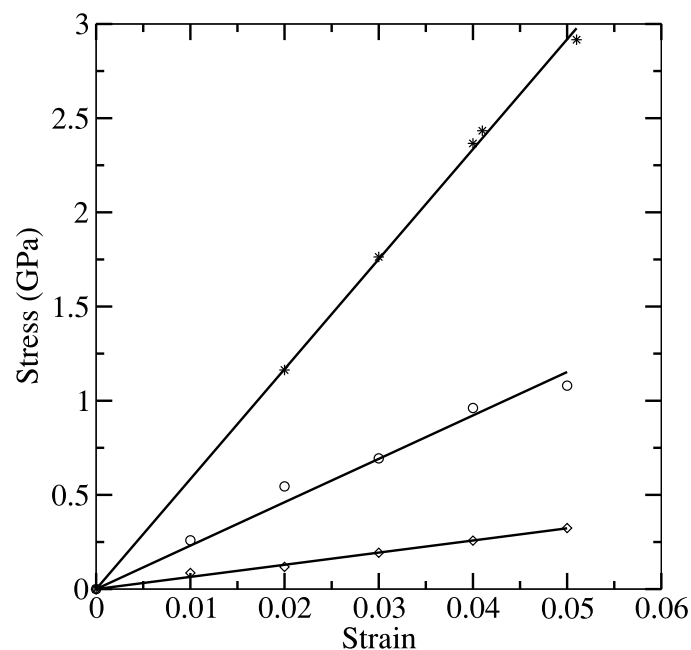


Fig. 7. The stress (σ_{axial})-strain (ϵ_{axial}) relation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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