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OPTICAL EXCITATIONS IN HEXAGONAL NANONETWORK MATERIALS

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Optical excitations in hexagonal nanonetwork materials, for example, Boron–Nitride (BN) sheets and nanotubes, are investigated theoretically. Exciton dipoles directed from the B site to the N site are considered along the BN bond. When the exciton hopping integral is restricted to the nearest neighbors, two flat bands of excitons appear. The symmetry of these exciton bands is optically forbidden. Possible relations with experiment are discussed.

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The hexagonal nanonetwork materials composed of atoms with ionic characters, for example, Boron–Nitride (BN) sheets and nanotubes [1, 2], have been intensely investigated. They are intrinsic insulators with the energy gap about 4 eV, as the preceding band calculations have indicated [3, 4]. The possible photogalvanic effects depending on the chiralities of BN nanotubes have been proposed by the model calculation [5]. Although not many optical measurements in the BN systems have been reported, it is quite interesting to predict condensed matter properties of the hexagonal nanonetwork materials.

In this paper, we investigate optical excitation properties in BN systems. The bonding is positively polarized at the B site and is negatively polarized at the N site. There is a permanent electric dipole moment along the BN bond directed from the B site to the N site. When we assume the one-orbital model [5] as shown in Fig. 1, the energy of the highest occupied atomic orbital of N is larger than that of B and the energy of the lowest unoccupied orbital of B is smaller than that of N. There is the band gap

$$\Delta \equiv \varepsilon_B - \varepsilon_N \sim 4 \text{ eV}$$

(see [3, 4]). Low-energy optical excitations are the excitations of electron–hole pairs between the higher occupied states of N and the lower unoccupied states of B atoms. The presence of the dipole moments gives rise to strong excitonic properties illustrated in Fig. 2.

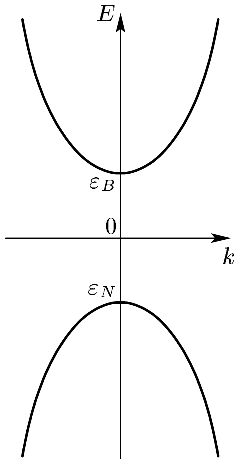

Fig. 1. The one-orbital model for low-energy dispersions of the BN network

In what follows, we discuss optical excitations in hexagonal nanonetwork materials, BN sheets and nanotubes. We show that two flat bands of excitons, which are optically forbidden, appear in the energy dispersions. Possible relations with experiments are discussed.

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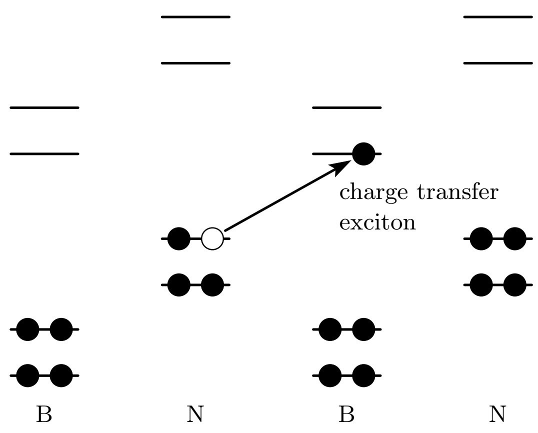

Fig. 2. Optical excitations along the BN alternations

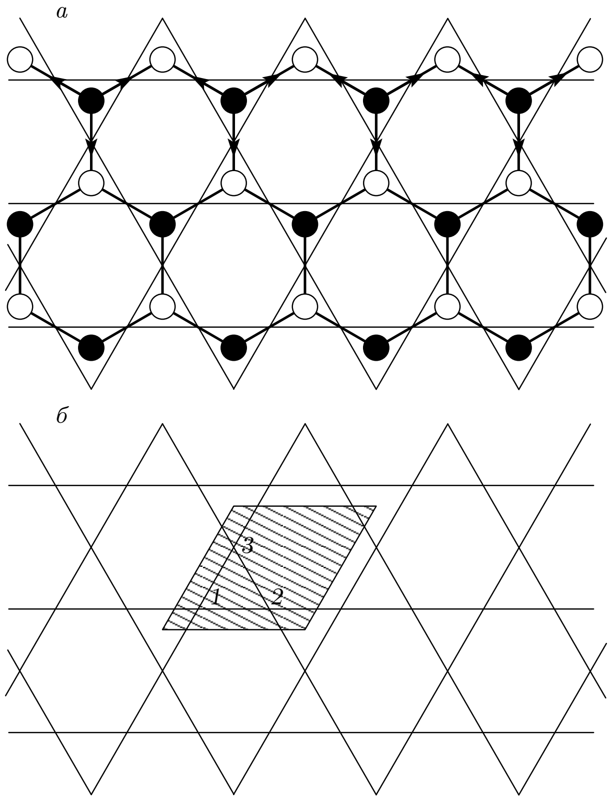

Fig. 3. a — The hexagonal nanonetwork of boron (full circles) and nitrogen sites (open circles). Several arrows indicate the directions of dipole moments, and the thin lines represent the conjugate Kagomé lattice network. b — The Kagomé lattice extracted from Fig. a. The shaded area is the unit cell, which has three lattice points indicated with numbers

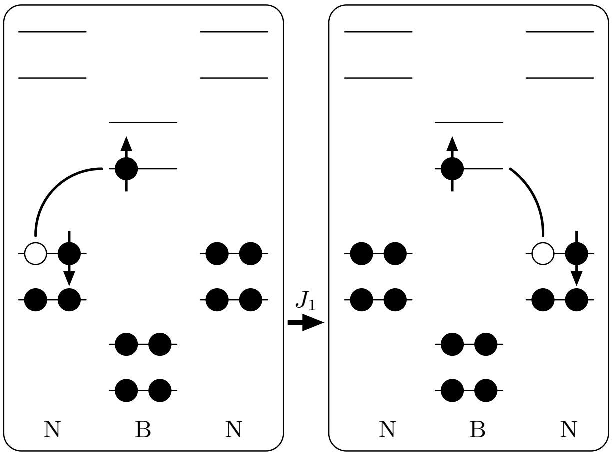

Fig. 4. The type 1 interaction J_1 that conserves an excited spin

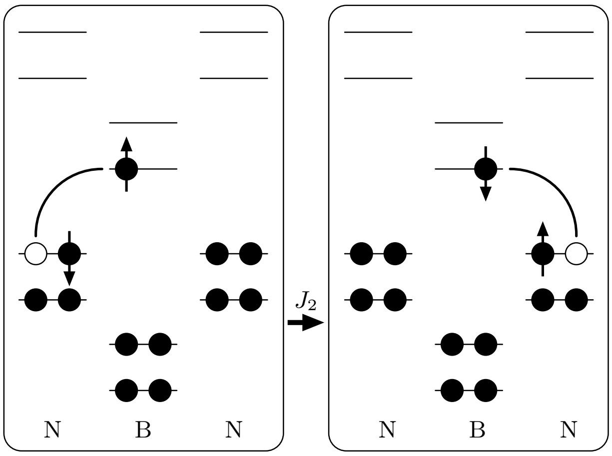

Fig. 5. The type 2 interaction J_2 where an excited spin flips

The interactions between the electric dipole moment along the BN bond has the strongest interaction strengths when the exciton hopping integral is restricted to the nearest neighbor dipoles. In Fig. 3a, the B and N atoms are represented by full and open circles, respectively. We assume the one-orbital Hubbard model with the hopping integral of electrons t, the on-site repulsion U, and the energy difference Δ between the B and N sites. After second-order perturbations, we obtain the nearest-neighbor interactions

$$J_1 = \frac{t^2}{-\Delta + U}$$

for the conserved excited spin (type 1 interaction) and

$$J_2 = \frac{t^2}{\Delta} + \frac{t^2}{-\Delta + U}$$

in the case where the spin of the excited electron flips (type 2 interaction). The meaning of the interactions J_1 and J_2 is illustrated in Figs. 4 and 5, respectively. When the condition $U > \Delta$ applies, J_1 and J_2 become positive. We discuss this case first, and comment on the case where J_1 and J_2 are negative afterwards. The interactions are present along the thin lines in Fig. 3*a*. The several arrows show the directions of dipole moments. After the extraction of the interactions J_1 and J_2, there remains the two-dimensional Kagomé lattice shown in Fig. 3*b*. As described in [6], the Kagomé lattice is obtained as a line graph of the hexagonal lattice. Therefore, the optical excitation hamiltonian becomes

$$H = \sum_{\langle i,j\rangle} \sum_{\sigma=\alpha,\beta} J_1(|i,\sigma\rangle\langle j,\sigma| + \text{H.c.}) + \\ + \sum_{\langle i,j\rangle} J_2(|i,\alpha\rangle\langle j,\beta| + |i,\beta\rangle\langle j,\alpha| + \text{H.c.}), \quad (1)$$

where the indices i and j denote the vertex points of the Kagomé lattice and the sum is taken over the nearest neighbor pairs $\langle i,j\rangle$ and the excited spin σ. The unit cell has three lattice points *1*, *2*, and *3*, as shown in Fig. 3*b*.

The model has six eigenenergies that are expressed in terms of wave numbers $\mathbf{k} = (k_x, k_y)$ as

$$E = \begin{cases} -2(J_1+J_2), \\ (J_1+J_2)\left\{1 \pm \sqrt{1+4\cos(k_x b/2)[\cos(k_x b/2)+\cos(\sqrt{3}k_y b/2)]}\right\}, \\ 2(-J_1+J_2), \\ (J_1-J_2)\left\{1 \pm \sqrt{1+4\cos(k_x b/2)[\cos(k_x b/2)+\cos(\sqrt{3}k_y b/2)]}\right\}, \end{cases} \quad (2)$$

where the two-dimensional x and y axes are defined as usual in Fig. 3, $b = \sqrt{3}a$ is the unit cell length of the Kagomé lattice in Fig. 3*b*, and a is the bond length in Fig. 3*a*. The dispersion relations are shown in Fig. 6 for the representative dimensionless parameters $J_1 = 1$ and $J_2 = 2$ that correspond to the case where $U = 2t$ and $\Delta = t$ in the second-order perturbation relations with $t = 1$. There appears a dispersionless band (triplet state) with the lowest energy $-2(J_1+J_2)$ when J_1 and J_2 are positive. There is another dispersionless band (singlet state) at the higher energy $2(-J_1+J_2)$. The other four bands have dispersions that are similar to those of the two-dimensional network of electrons on graphite [7]. In fact, with the electron hopping integral of graphite denoted as t, the dispersion is

$$E = \pm t\sqrt{1+4\cos(k_x b/2)\left[\cos(k_x b/2)+\cos(\sqrt{3}k_y b/2)\right]}. \quad (3)$$

We note that the x and y axes are interchanged compared with the definitions used in [7].

Such appearance of the flat band, for example, in the Kagomé lattice, has been discussed in the literature [6, 8] from the standpoint of possible ferromagnetism. In the present case, the lowest optical excitation band becomes flat in the honeycomb BN plane when the interactions J_1 and J_2 are positive. When the BN plane is rolled up into nanotubes, the flat band is also dispersionless. The interesting properties of excitons on the Kagomé lattice have been investigated recently [9].

To discuss how the excitons appear in optical experiments, we must consider symmetries of the wave functions. The most interesting part is the wave function of the lowest excitons with the energy $-2(J_1+J_2)$ when J_1 and J_2 are positive.

Solving the eigenvalue problem at the wave number $\mathbf{k} = (0,0)$,

$$\begin{pmatrix} 0 & 0 & 2J_1 & 2J_2 & 2J_1 & 2J_2 \\ 0 & 0 & 2J_2 & 2J_1 & 2J_2 & 2J_1 \\ 2J_1 & 2J_2 & 0 & 0 & 2J_1 & 2J_2 \\ 2J_2 & 2J_1 & 0 & 0 & 2J_2 & 2J_1 \\ 2J_1 & 2J_2 & 2J_1 & 2J_2 & 0 & 0 \\ 2J_2 & 2J_1 & 2J_2 & 2J_1 & 0 & 0 \end{pmatrix} \Psi = E\Psi, \quad (4)$$

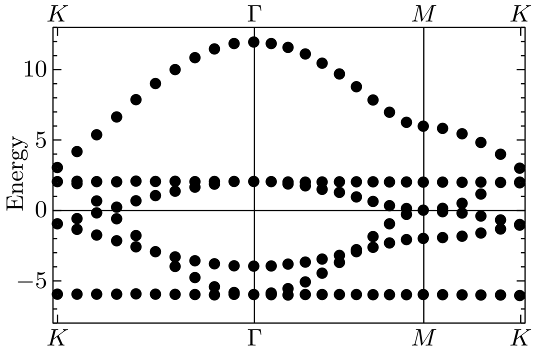

Fig. 6. Energy dispersions for the dimensionless parameters $J_1 = 1$ and $J_2 = 2$

we obtain the two-fold degenerate solutions for the energy $E = -2(J_1 + J_2)$,

$$\Psi^\dagger = \frac{1}{2}\Big(\; 1, \;\; 1, \;\; -1, \;\; -1, \;\; 0, \;\; 0 \; \Big), \tag{5}$$

and

$$\Psi^\dagger = \frac{1}{2\sqrt{3}}\Big(\; 1, \;\; 1, \;\; 1, \;\; 1, \;\; -2, \;\; -2 \; \Big). \tag{6}$$

It follows that the spin of these states corresponds to a triplet. Similarly, we obtain the solutions for the energy $E = 2(-J_1 + J_2)$,

$$\Psi^\dagger = \frac{1}{2}\Big(\; 1, \;\; -1, \;\; -1, \;\; 1, \;\; 0, \;\; 0 \; \Big), \tag{7}$$

and

$$\Psi^\dagger = \frac{1}{2\sqrt{3}}\Big(\; 1, \;\; -1, \;\; 1, \;\; -1, \;\; -2, \;\; 2 \; \Big). \tag{8}$$

The spin alignment of these states corresponds to a singlet.

The symmetry of solution (5) of the up or down spin sector is shown in Fig. 7*a*, and that of solution (6) is displayed in Fig. 7*b*. We find that both wave functions are symmetric under spatial inversion, and therefore they have the symmetry gerade. The transition to the flat band exciton is optically forbidden. Such properties might result in interesting optical measurements in hexagonal nanonetwork materials. Similarly, the symmetry of states (7) and (8) is gerade with respect to the spatial inversion.

Finally, the dispersions of excitons in the case where $J_1 < 0$ and $J_2 < 0$ are of interest. Representative dispersions are shown in Fig. 8 for the dimensionless parameters $J_1 = -2$ and $J_2 = -1$. These correspond to $U = 0.5t$ and $\Delta = t$ with $t = 1$ in the formula of the second-order perturbations J_1 and J_2. The energy

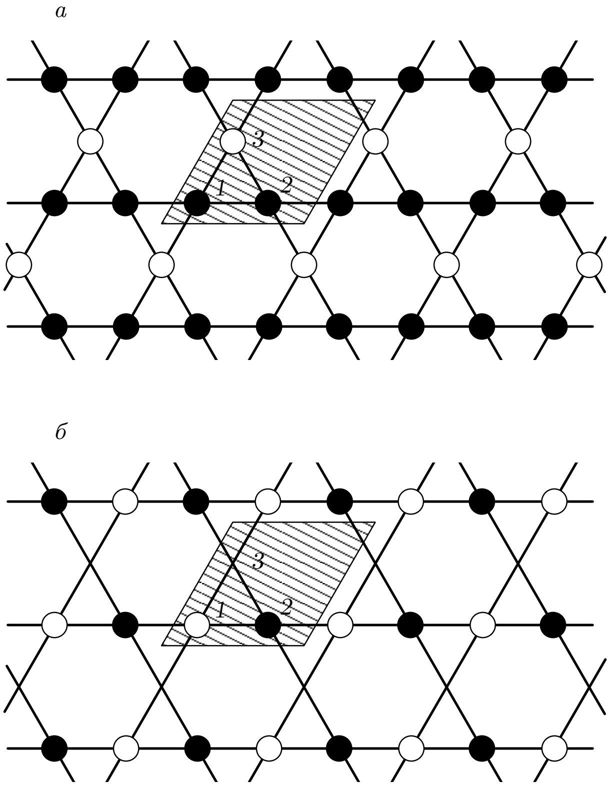

Fig. 7. Symmetries of two wave functions at $E = -2(J_1 + J_2)$ for the spin-up or down sector. The full and open circles indicate positive and negative values at the lattice point, respectively. If the value at the lattice point is zero, nothing is shown there. The numbers *1*, *2*, and *3* in the unit cell correspond to the first, third, and fifth (second, fourth, and sixth) elements for the up (down) spin sector of the wave function Ψ in Eq. (4), respectively

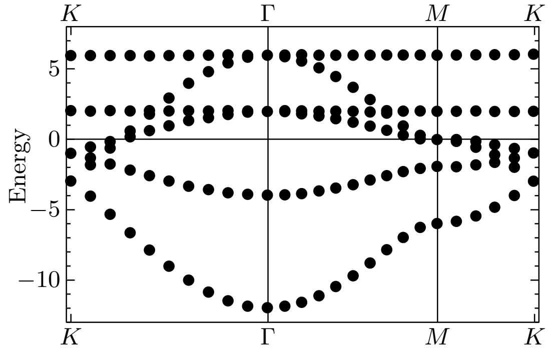

Fig. 8. Energy dispersions for the dimensionless parameters $J_1 = -2$ and $J_2 = -1$

band structures are almost interchanged between top and bottom compared with those in Fig. 6. There is a flat band at the top of the excitonic bands. The lowest exciton has a finite dispersion, but this state is still an optically forbidden triplet.

The optically forbidden transition is known in the C_{60} molecules [10]. The luminescence from the lowest exciton has a long lifetime due to the forbidden transition nature [11, 12]. We have analyzed possible phonon couplings in the luminescence spectra [13]. A formalism similar to the one in this paper could be applied to systems with honeycomb or Kagomé network materials, where neighboring interactions with dipoles are effective.

In summary, optical excitations in BN sheets and nanotubes have been investigated theoretically. We have shown that two flat bands of excitons, which are optically forbidden, appear in the energy dipsersions. Possible relations with experiments have been discussed.

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