ELECTRONIC ENERGY BAND STRUCTURE OF MOLECULAR CRYSTALS MCI · $(TCNQ)_2$ AND ITS RELATIONSHIP WITH THE ELECTRICAL CONDUCTION*

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ABSTRACT

The structure of electronic energy bands, electric charge distribution and the amount of charge transfer of molecular crystals 1-MCI · $(TCNQ)_2$ (I) and 2-MCI · $(TCNQ)_2$ (II) have been studied. The results are: (i) The dominant contributions to the electrical conductivities for crystals I and II are from TCNQ molecular columns, and the charge carriers are electrons. (ii) The electrical conduction is mainly due to the hopping of charge carriers between the seats of lattice. (iii) The considerable difference of the electrical conductivities between crystals I and II is due to the differences between (a) the concentrations of charge carriers $n^C_{AI} = 0.9988 - |e|$/cell and $n^C_{AII} = 0.0340 - |e|$/cell; (b) the widths of the energy bands $\Delta E^{LU}_{AI} = 0.88$ eV and $\Delta E^{LU}_{AII} = 0.040$ eV; (c) the first derivative of E with respect to k, $(dE/dk)^{LU}_{K_F AI} = 0.27$ eV · Å and $(dE/dk)^{LU}_{K_F AII} = 0.0048$ eV · Å; and (d) the difference of energy barriers for the hopping of charge carriers $\epsilon_{II} - \epsilon_I = 2.5$—$8.8$ kJ/mol.

Keywords: structure of electronic energy bands, energy bands and the electrical conductivities, molecular crystal, MIC · $(TCNQ)_2$.

Cursory consideration of the structure parameters of charge transfer complex crystals 1-MCI · $(TCNQ)_2$ [1-methylcinnaline · $(TCNQ)_2$] (I) and 2-MCI · $(TCNQ)_2$ [2-methylcinnaline · $(TCNQ)_2$] (II)[1,2] might lead one to anticipate the similar electrical conductivities for them. In fact, the difference between the room-temperature electrical conductivities of I and II, $\sigma^{RT}_I = 1$—2×10^1 and $\sigma^{RT}_{II} = 1$—$9 \times 10^{-3}(\Omega \cdot cm)^{-1}$[1,2], is considerable. This phenomenon promoted our interest of searching for the causes for such difference from quantum chemistry point of view.

In this paper, the structure of electronic energy bands and the electrical charge distribution for crystals I and II have been calculated, and the factors causing the difference between σ^{RT}_I and σ^{RT}_{II} have been analyzed. Finally, the mechanism of the electrical conduction has been discussed.

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I. Model, Method and Principle of Calculation

In crystals I and II, the packings of molecules MCIs and TCNQs appear in relative independent molecular columns respectively[1,2]. Because of the charge transfer between molecular columns, usually, the kind of charge carriers and the behavior of electrical conduction are different for columns of the electronic donor and acceptor. Generally the intercolumn interaction is small[3,4] so that the electronic energy bands for columns of electronic donor and acceptor can be calculated independently without essential effects on the results[3]. Crystals I and II are of this case. According to Refs. [1] and [2], the model for calculation can be shown in Fig. 1.

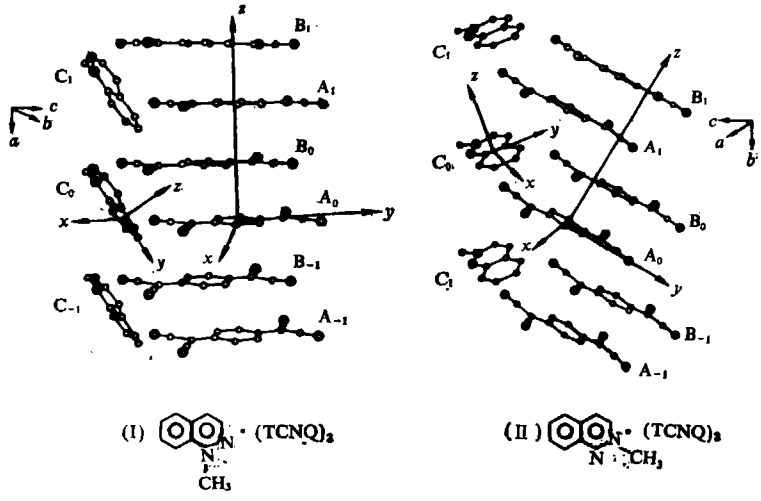

Fig. 1. Models of calculation.

The stoichiometrical ratio of MCl and TCNQ in crystals I and II is 1:2, so that (MCI) and ($TCNQ_A \cdot TCNQ_B$) are taken as structure units for columns MCI and TCNQ respectively. Tight binding[5] and EHMO[6] methods and STO are used in the calculation. The Hückel correlative coefficient $K = 1.75$; the orbital exponents ζ_C, ζ_N, ζ_H are 1.6250, 1.9500, 1.3000, and the valence ionization potentials I_{CS}, I_{NS}, I_{HS} are -21.4000, -26.0000. and -13.6000 eV; and I_{CP}, I_{NP} are -11.4000 and -13.4000 respectively. In order to investigate the charge transfer and the overlap between orbitals, the super-molecules ($TCNQ_{A_0} \cdot TCNQ_{B_0}$), ($TCNQ_{B_0} \cdot TCNQ_{A_1}$) and ($MCI_{C_0} \cdot TCNQ_{A_0} \cdot TCNQ_{B_0}$) in both crystals I and II are also calculated.

For a charge transfer crystal with relative independent molecular columns of the electronic donor and acceptor the electrical conductivity can be expressed as Eq. (1)

$$\sigma = n_D^c N_C e_D \mu_D + n_A^c N_C e_A \mu_A, \tag{1}$$

where n^c denotes the number of charge carriers per cell (carr/cell), and N_C the number of cells per cm^3 (cell/cm^3). e is the amount of electric charge per charge carrier, and for an electron and a hole the charges are $-|e|$/carr and $|e|$/carr respectively. μ stands for the mobility of charge carriers (cm^2/s.V). The subscripts D and A denote the molecular columns of the electronic donor and acceptor.

The creation of charge carriers in a charge transfer complex molecule is mainly due to the transfer of a certain part of electric charge from the band HO of the donor column to the band LU of the acceptor column. In Refs. [7] and [1] the amount of charge transfer is estimated by comparison of the corresponding bond lengths in isolated ion $TCNQ^-$ and molecule TCNQ. However, the bond lengths of $TCNQ^-$ and TCNQ are under the influence of the surroundings, and usually are not located in the interval of the isolated $TCNQ^-$ and TCNQ, just as the case in the present paper. The reliable method to obtain the amount of charge transfer is the calculation with quantum chemistry.

According to the theory of Fröhlich and Sewell. the mobility of charger carriers for a charge transfer crystal can be shown by[8,9]

$$\mu = \frac{e\tau(E_F)L^2(\Delta E)^2}{\hbar^2 k_B T}, \tag{2}$$

where $\tau(E_F)$ stands for the relaxation time at the Fermi surface, ΔE for the width of corresponding frontier energy band k_B for Boltzmann constant, T for absolute temperature, $\hbar = h/2$ for Planck constant and L for the length of cell in the direction of conduction. Usually, when an electric charge carrier migrates from a molecule to an adjacent one, it must obtain an energy greater than the potential barrier ε similar to the hopping in ionic crystals[10,11]. Eq. (2) can be expressed in the form of Eq. (2) in Refs. [10]—[13]:

$$\mu = \frac{e\tau_0(E_F)L^2(\Delta E)^2}{\hbar^2 k_B T} e^{-\varepsilon/k_B T}. \tag{2'}$$

When $\varepsilon \to 0$, i.e. the mean free path l of charge carriers is long enough, the migration of charge carriers can be described with band mechanism.

According to solid state physics[14], the relationship between the relaxation time τ and (dE/dk) for atomic crystals can be shown by

$$\tau = \frac{A}{B}\left(\frac{dE}{dk}\right), \tag{3}$$

where $A = NM\hbar\bar{c}^2/k_B T$, $B = \int J^2(E, \eta)(1 - \cos\eta)2\pi k^2 \sin\eta d\eta$. M stands for atomic weight, N for the number of cells under consideration, $\bar{c}$ for the mean speed of the elastic wave, J for the summation which is related to the total transition probability, and η for the scattering angle. For molecular crystals Eq. (3) should be true, but A and B will be different from those of atomic crystals. For a quasi one-dimensional molecular crystal, the scattering angle η will be either 0 or π, and the B in Eq. (3) will be reduced to

$$B = 2J^2(E). \tag{4}$$

II. Structure of Electronic Energy Bands and the Distribution of Charge

The electronic energy bands are shown in Fig. 2. Because the electrical conduction of crystal is related to the bands near the Fermi surface only, just frontier bands and sub-frontier bands are given. For the convenience of calculation, the dimensionless scale parameter α is used instead of the wave vector k. For crystals I and II, there

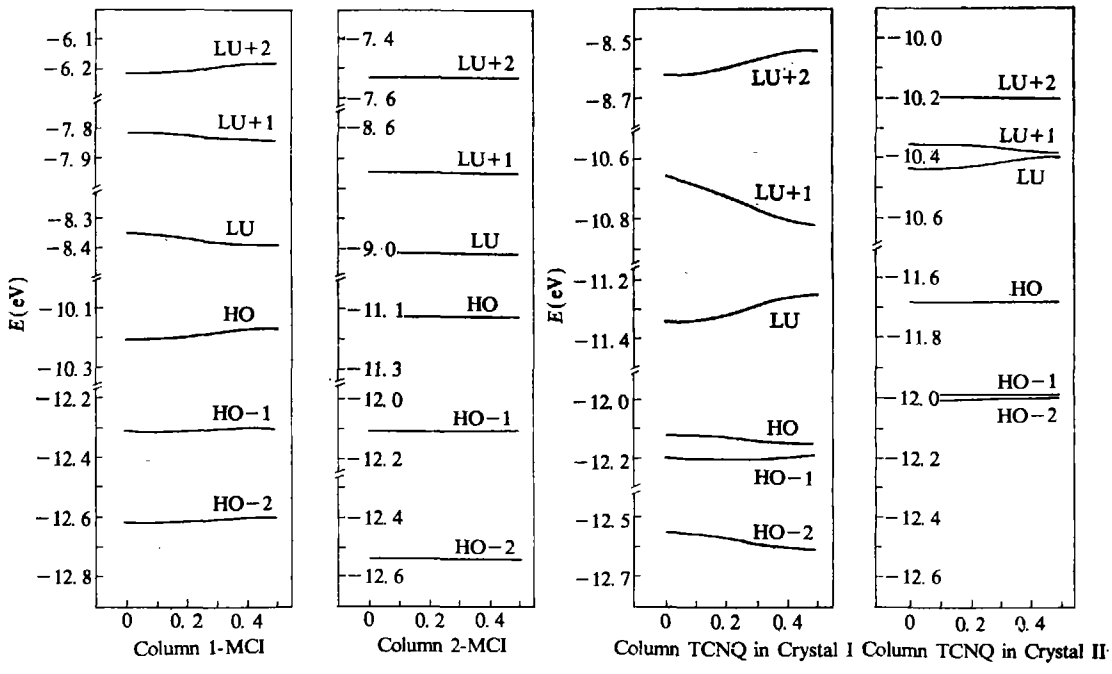

Fig. 2. Electronic energy bands of crystals I and II.

are $2\pi\alpha = ka$ and $2\pi\alpha = kb$, where a and b are the length of the cell in the direction of electrical conduction.

The intermolecular total overlap of crystals I and II are shown in Table 1, and the numbers of molecules are shown in Fig. 1. One can see that the algebra summations (S) of the overlap of atomic orbitals are much smaller than the absolute ones ABS (S). This indicates that because of the packing condition, most of the overlaps between atomic orbitals are cancelled by each other. The correct net overlap should be obtained from concrete calculation and the cursory estimation[3,11] usually leads to wrong results. It can also be seen from Table 1 that the net overlap of the molecular column TCNQ $S(B_0, A_1)$ in crystal II is smaller than that in crystal I, and it causes the bands in crystal II to be narrower than those in crystal I[15]. The distances between molecules MCIs in both crystals I and II are much longer than those between TCNQs, so that the overlaps $S(C_0, C_1)$s are quite small, and the corresponding bands are quite narrow too, especially in crystal II. Because of the orientation of molecules 2-MCIs, the bands are even narrower.

The quantities of charge transfers from the band HO of molecular column MCI to the band LU of column TCNQ are $0.9988 - |e|$/cell and $0.0340 - |e|$/cell for crystals I and II respectively. These results are consistent with the relative positions between the band HO of column MCI and the band LU of column TCNQ for both crystals. The corresponding concentrations of charge carriers are $n^c_{DI} = 0.0012$ carr/cell; $n^c_{AI} = 0.9988$ carr/cell; and $n^c_{DII} = 0.9660$ carr/cell; $n^c_{AII} = 0.340$ carr/cell. The numbers of cells per cm^3 are $N_{CI} = 1.46 \times 10^{21}$ cell/cm^3 and $N_{CII} = 1.44 \times 10^{21}$ cell/cm^3. As shown in Fig. 3, for crystal I, the Fermi surface goes through the bottom

Table 1

Intermolecular Overlaps for Crystals I and II

Crystals	Overlaps	$S(A_0,B_0)$	$S(B_0,A_1)$	$S(A_0,C_0)$	$S(B_0,C_0)$	$S(C_0,C_1)$
I	S	−0.3642	−0.0042	0.0164	0.1236	0.0031
	ABS(S)	6.2962	5.7988	0.3624	1.2855	0.8453
II	S	−0.3615	−0.0276	0.2981	−0.0768	0.0000
	ABS(S)	4.4071	2.0036	2.4923	0.5216	0.0000

Note: A, $TCNQ_A$; B, $TCNQ_B$; C, MCI_C; S, $\sum_i S_i$; ABS(S), $\sum_i |S_i|$

of band HO of column 1-MCI and the middle of band LU of column TCNQ, and for crystal II, the Fermi surface goes through the middle of band HO of column 2-MCI and the bottom of band LU of column TCNQ. Because there is $(d^2E/dk^2)^{k_F} > 0$ for the bands mentioned above, the charge carriers should be electrons.

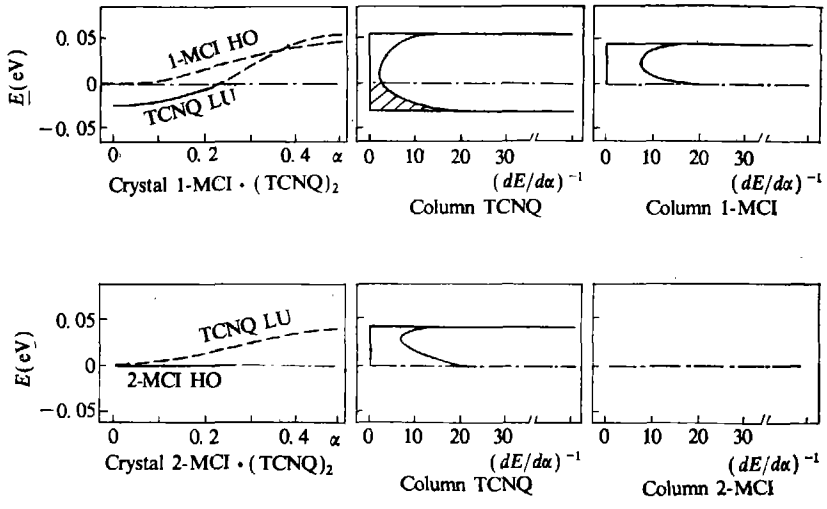

Fig. 3. The band structure and the density of states of crystals I and II near Fermi surface. ——, Occupied bands; ----, empty bands; —·—, Fermi surface; shadow, occupied states.

After the charge transfer, the molecular columns of the electronic donor and acceptor obtain positive and negative charges respectively. The distribution of electric charge among atoms in a cell is the fine structure of charge density wave within a periodic unit, as shown in Fig. 4.

When the crystal is under the influence of a certain electrical field, the state k of system will be changed, and the corresponding motion of electrons and holes in the unfilled bands will occur. The relationship between the distribution of the amount of charge transfers and the wave vectors $\Delta(\Delta q)_k - k$ has been calculated. The corresponding $\Delta(\Delta q)_k$ for crystal II is much smaller than that of crystal I. This

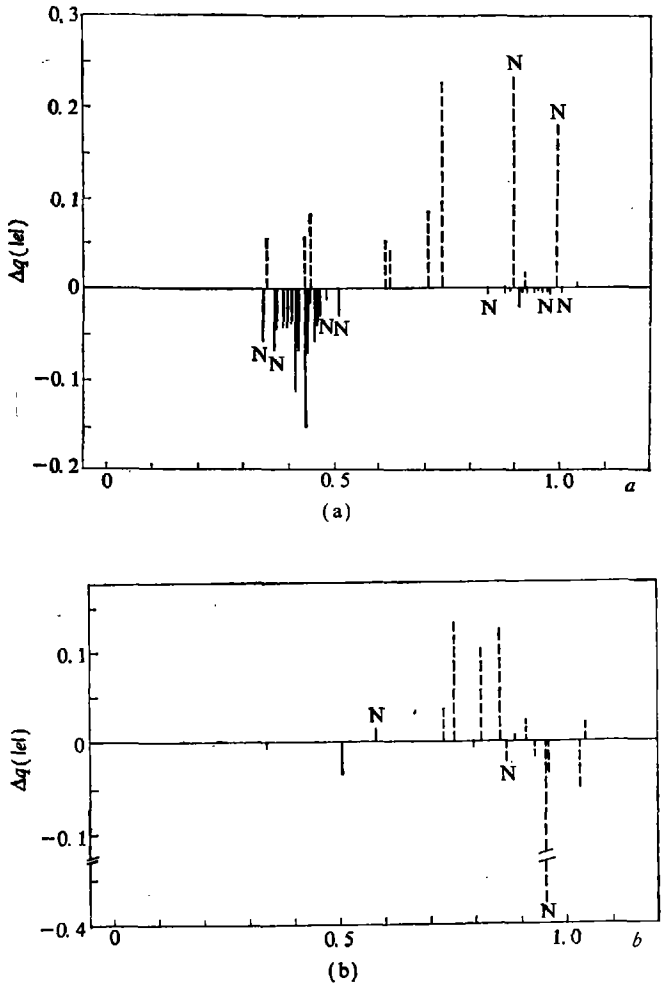

Fig. 4. Distribution of charge transfer within a cell.
(a) Cell 1-MCI · $(TCNQ)_2$, (b) cell 2-MCI · $(TCNQ)_2$
N, Atom nitrogen; ——, Δq in MCI; others, atom carbon. ----, q in TCNQ.

result is consistent with the fact of $\sigma_{II}^{RT} \ll \sigma_{I}^{RT}$.

III. Analysis of Factors Which Affect the Electrical Conductivities of Crystals and the Conclusions

The results for concentraction of charge carriers n^c, the width of energy bands ΔE and the $(dE/d\alpha)_{\alpha_F}$ for crystals I and II are shown in Table 2.

From Eqs. (1)—(4), the contribution of a molecular column to the electrical conductivity of the crystal can be shown as follows:

$$\sigma = N_C \frac{A}{B} \frac{e^2}{\hbar^2 k_B T} n^c \left(\frac{dE}{dk}\right)_{k_F} L^2(\Delta E)^2 e^{-\varepsilon/k_B T}. \tag{5}$$

According to the parameters of crystal structure, there is $N_{C(I)} \simeq N_{C(II)}$. Since the

Table 2

Comparison of Factors Which Affect the Electrical Conductivities of Crystals I and II

	Crystal I		Crystal II	
	coln 1-MCI	coln TCNQ	coln 2-MCI	coln TCNQ
n_D^c(carr/cell)	1.2×10^{-3}		9.7×10^{-1}	
n_A^c(carr/cell)		9.988×10^{-1}		3.4×10^{-2}
ΔE (eV)	4.6×10^{-2}	8.8×10^{-2}	1.3×10^{-4}	4.0×10^{-2}
$(dE/d\alpha)_{\alpha_F}$ (eV)	2.5×10^{-4}	2.6×10^{-1}	0.00000	3.9×10^{-3}
σ'_D/C((eV)^3 Å^3/cell)	2.7×10^{-8}		0.00000	
σ'_A/C((eV)^3 Å^3/cell)		8.8×10^{-2}		1.5×10^{-5}

Note: $\sigma' = C \cdot n^c(dE/k)_{k_F} \cdot L^2 \cdot (\Delta E)^2$; $(dE/dk) = (1/2\pi)(dE/d\alpha)$; $L_I = 6.5157$ (Å); $L_{II} = 7.5987$ (Å).

super-molecules 1-MCI · $(TCNQ)_2$ and 2-MCI·$(TCNQ)_2$ are isomers, there is $A_I = A_{II}$. For atomic crystals, B indicates the change of the atom-field within a cell. For molecular crystals, B will be quite complicate to analyze quantitively, but because of the similar structure of crystals I and II, the approximation $B_I \simeq B_{II}$ can be taken approximately. After the collection of the factors, which are common for crystals I and II, into C, Eq. (5) can be shown as Eq. (6)

$$\sigma = Cn^c\left(\frac{dE}{dk}\right)_{k_F} L^2(\Delta E)^2 e^{-\varepsilon/k_BT}, \tag{6}$$

when $\varepsilon \to 0$

$$\sigma' = Cn^c\left(\frac{dE}{dk}\right)_{k_F} L^2(\Delta E)^2. \tag{6'}$$

From the value σ'/C for each molecular column, shown in Table 2, it can be seen that the main contributions to the electrical conductivities are from molecular column TCNQs for both crystals I and II. The value of σ'_I/σ'_{II} is shown in Table 3.

Table 3

Comparison of the Calculated and Determined Values of σ_I/σ_{II}

(σ'_I/σ'_{II}) Cal.	(σ_I/σ_{II}) Cal.[a)]	(σ_I/σ_{II}) Det.[1,2]
6.0×10^3	1.6×10^4—1.8×10^5	1.1×10^3—2.0×10^4

a) $\sigma_I/\sigma_{II} = (\sigma'_I/\sigma'_{II}) \cdot e^{\Delta\varepsilon/k_BT}$; $T = 300$ K; $\Delta\varepsilon = \varepsilon_{II} - \varepsilon_I = 2.5$—$8.8$ kJ/mol $= 2.5$—9.0×10^{-2} eV/carr.

As for $\varepsilon > 0$, according to the σ-T data[1], the $(\varepsilon_{II} - \varepsilon_I)$ can be obtained as shown in Fig. 5 and Table 3. The calculated ($T = 300$ K) and determined values of σ_I/σ_{II} are also shown in Table 3.

Considering that the charge transfer complex molecular crystal is much more complicate than the atomic crystal, some approximations were taken in the above analysis and calculation; and because of the difficulties in determination, usually

there are some discrepancies among the reported values of electrical conductivities for the same material. It may be regarded that the consistency between the calculated and determined values shown in Table 3 is satisfactory. According to the results mentioned above, the conclusion reached in this paper is reasonable, i.e. the essential difference between the electrical conductivities of crystals I and II is from the essential differences of the concentrations of charge carriers, the widths of corresponding frontier energy bands, (dE/dk) and the potential barriers between crystals I and II.

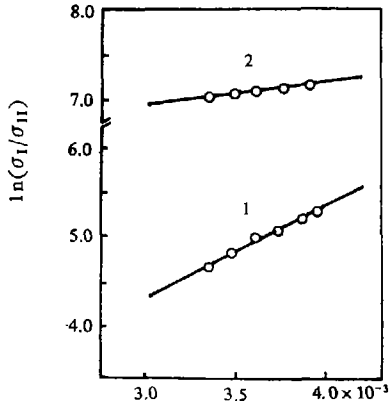

Fig. 5. $\ln(\sigma_I/\sigma_{II})-1/T$.
1, $\Delta\varepsilon\sim8.8$ kJ/mol; 2, $\Delta\varepsilon\sim2.5$ kJ/mol.

Finally, one can make some further estimations. The mechanism of migration of charge carriers can be of band and hopping under the same condition[11]. From the relationship between the electrical conductivities σ and the mean free path l of the charge carriers[3], there are $l_I = 2.8 \times 10^{-1}$ Å and $l_{II} = 1.1 \times 10^{-4}$ Å. Both of them are much smaller than the length of the axis of the cell in the conducting direction, therefore the migration of charge carriers is mainly by hopping between the seats of the lattice. Considering the influence of T in the pre-exponent factor on σ is much smaller than that of T in the exponent factor by Eq. (5), the barriers $\varepsilon_I \sim 6.28$ kJ/mol and $\varepsilon_{II} \sim 8.37$ —14.64 kJ/mol can be obtained. There is $\varepsilon_{II} \sim 2\varepsilon_I$. but both of them are smaller than the barrier in chemical reaction (41.84—418.4 kJ/mol), belonging to van der Waals interaction.

References

[1] Zhu Daoben et al., *Mol. Cryst. Liq. Cryst.*, **128**(1985), 321.
[2] Qian Minxie, Zhu Naijue & Zhu Daoben, *Jiegou Huaxue* (*J. Struct. Chem.*), **3**(1984), 79; 83.
[3] Berlinsky, A. J., *Contemp. Phys.*, **17**(1976), 331.
[4] Imaede, K. et al., *Bull. Chem. Soc. Jpn.*, **62**(1989), 372.
[5] Whangbo, M.-H., Hoffmann, R. & Woodward, R. B., *Proc. Roy. Soc.*, London, **A366**(1979), 23.
[6] Hoffmann, R., *J. Chem. phys.*, **39**(1963), 1397.
[7] Konno, M. & Saito, Y., *Acta Cryst.*, **B37**(1981), 2034.
[8] Fröhlich, H. & Sewell, G. L., *Proc. Phys. Soc.*, London, **74**(1959), 643.
[9] Pigon, K. & Chojnacki, H., in *Molecular Interactions* (Eds. Ratajczak, H. & Orville-Thomas, W. J.), Vol. 2, John Wiley and Sons, New York, 1981, p. 451.

[10] 黄 昆、韩汝琦，固体物理学，高等教育出版社，1988，p. 529.
[11] Yan Ji-min, *Solid State Comm.*, **71**(1989), 135.
[12] Mott, N. F., *Adv. Phys.*, **16**(1967), 49.
[13] Glarum, S. H., *J. Phys. Chem. Solids*, **24**(1963), 1577.
[14] 黄 昆、韩汝琦，固体物理学，高等教育出版社，1988，p. 153.
[15] a) 严继民、张启元，化学学报，**40**(1982)，774;
b) ————，科学通报，**23**(1983)，536.
c) Yan Jimin & Zhang Qiyuan, *Kexue Tongbao*, **29**(1984), 475.