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Charge-transfer Interaction and Ground-state Energy Stabilization in Crystalline Complex Ion Radical Salts

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Synopsis. Although predominant cohesive energy is Madelung energy, the ground state of crystalline complex ion radical salt is further stabilized by the charge-transfer interaction between neutral molecule and ion radical, together with that between ion radicals. The magnitude of this stabilization energy was estimated with (Phenothiazine)$_2^{+\cdot}$ Br$^-$.

In crystalline simple ion radical salts, the planar ion radical molecules are known to form, in themselves, a segregated stacking into columns so as to make a large overlap between their half-occupied molecular orbitals.[1] Much attention has been paid to the prominent optical and magnetic properties of such ion radical salts.[1-6] In their optical properties, charge-transfer absorption due to the transition of unpaired electron between ion radical molecules appear in the low-energy region. As for the magnetic properties, antiferromagnetic spin exchange interaction acts between adjacent ion radicals, so that such a salt is considered as one-dimensional Heisenberg antifferomagnet. In previous papers,[2,3] we applied one-dimensional half-occupied Hubbard model to the segregated stack of ion radical molecules. This model is a simplification of the real crystal and is described by two parameters I and T. $T(<0)$ is the transfer matrix element of an unpaired electron which describes hopping between adjacent molecular ion radical sites, while I is the on-site Coulomb repulsion between two electrons with up and down spins on the same molecule. This model could well explain the reason why the charge-transfer absorption is observable in such ion radical salts.[2] The applicability of the Hubbard model is further justified by the fact that the one-dimensional half-occupied Hubbard model with $I \gg |T|$ becomes equivalent to one-dimensional Heisenberg antiferromagnet with exchange interaction $J=2T^2/I$.[7] Then, the ground-state energy of the one-dimensional system of ion radicals can be given by $E=-2NJ\ln 2=-(4NT^2/I)\ln 2$, where $N\rightarrow\infty$ is the number of ion radical molecules in the one-dimensional system.[3] This energy stabilization is caused by the charge-transfer interaction between unpaired electrons of adjacent ion radicals through non-zero $|T|$ value in segregated stack of ion radicals.

So far, we have considered simple ion radical salts, where each ion radical carries one unpaired electron. In the case of crystalline complex ion radical salts, the ion-radical and parent neutral molecules are known to stack together to form regular one-dimensional column, where each molecular site is occupied by less-than-one electron.[4-6] Then, we can apply regular one-dimensional less-than-half occupied Hubbard model to the segregated stack composed of ion-radical and neutral molecules in crystalline complex ion radical salts. Shiba and Klein-Seitz have shown that the magnetic susceptibility of a uniform stack of less-than-half occupied molecules (average number of unpaired electrons per site is $\rho<1$) is related to the magnetic susceptibility of a uniform stack of half-occupied molecules ($\rho=1$) in simple ion radical salt.[8,9] If the value of I is much larger than that of $|T|$, the less-than-half occupied one-dimensional Hubbard model becomes equivalent to an antiferromagnetic Heisenberg chain with exchange interaction,[10]

$$J=\frac{2T^2\rho}{I}\left(1-\frac{\sin 2\pi\rho}{2\pi\rho}\right). \tag{1}$$

Under the same condition, the lowest energy was also given by Shiba.[8] If we denote total number of molecular sites as N, the number of unpaired electrons is given by $N\rho$, and the lowest energy of the system, E, is expressed by

$$E/N|T| = -\left\{\frac{2}{\pi}\sin\pi\rho+\frac{4|T|\rho^2\ln 2}{I}\left(1-\frac{\sin 2\pi\rho}{2\pi\rho}\right)\right\}. \tag{2}$$

In the case of $\rho<1$, the E value of Eq. 2 is composed of two factors; one is the term, $E_1=-(2/\pi)N|T|\sin\pi\rho$, and the other, $E_2=-(4NT^2\rho^2/I)\ln 2\ (1-\sin 2\pi\rho/(2\pi\rho))$. The E_2 term is regarded as the stabilization energy due to the charge-transfer interaction between unpaired electrons. In terms of J in Eq. 1, E_2 is written as $-2NJ\rho\ln 2$. On the other hand, the E_1 term is characteristic of less-than-half occupied system. It becomes zero at $\rho=0$ or 1, but has the most negative value of $-(2/\pi)N|T|$ at $\rho=1/2$. E_1 is not a function of I, but is related only to $|T|$ and ρ. Therefore, E_1 corresponds to the stabilization energy due to the charge-transfer interaction between neutral and ion-radical molecules in one-dimensional system. If we consider the case of $\rho=1$, Eq. 1 is simply $J=2T^2/I$, and Eq. 2 is reduced to $E=E_2=-(4NT^2/I)\ln 2$ and $E_1=0$. As our model requires, the J and E values are found to be identical with those described previously in simple ion radical salt. In the case of half-occupied Hubbard model with $\rho=1$, each molecular site is occupied by one unpaired electron and there remains no neutral molecular site, so that there acts no charge-transfer interaction between neutral and ion-radical molecules in simple ion radical salts. This is the reason why $E_1=0$ at $\rho=1$. Therefore, the energy stabilization due to E_1 appears only in complex ion radical salts.

Next, we shall apply the above-mentioned approach to certain crystalline complex ion radical salt and estimate its ground-state stabilization energy. For purposes of comparison, we shall also examine the corresponding simple salt. For this purpose, we take simple cation radical salt of (Phenothiazine)$^{+\cdot}$ Br$^-$ and complex salt of (Phenothiazine)$_2^{+\cdot}$ Br$^-$. In previous papers,[6] we reported that the optical and magnetic properties of those phenothiazine (PT) cation radical salts were well explained by applying regular one-dimensional Hubbard model to the segregated stack of phenothiazines, and estimated the values of $I=12900\ \text{cm}^{-1}$ and $T\approx-2500\ \text{cm}^{-1}$ for the one-dimensional system of the simple salt of $\text{PT}^{+\cdot}\ \text{Br}^-$. Moreover, these parameter values could be commonly used for the one-dimensional system of the complex salt of $(\text{PT})_2{}^{+\cdot}\ \text{Br}^-$. Then, the average number of unpaired electrons per site and the number of phenothiazine sites are $\rho=1$ and $N=N_\text{A}$ (Avogadro number) for one mole of $\text{PT}^{+\cdot}\ \text{Br}^-$, respectively, while they are $\rho=1/2$ and $N=2N_\text{A}$ for one mol of $(\text{PT})_2{}^{+\cdot}\ \text{Br}^-$, respectively. In the case of the simple salt, by the use of $E=-(4NT^2/I)\ \ln 2$ together with the estimated I and T values, the stabilization energy due to the charge-transfer interaction between phenothiazine cation radicals was calculated to be $E=-16.0\ \text{kJ mol}^{-1}$. As for the complex salt, the stabilization energy, E, is given by two factors, E_1 and E_2. By using the E_2 equation together with $N=2N_\text{A}$, $\rho=1/2$, $I=12900\ \text{cm}^{-1}$ and $T\approx-2500\ \text{cm}^{-1}$, the value of E_2 was determined to be $-8.0\ \text{kJ mol}^{-1}$, whose magnitude was found to be just half of that of E in the simple salt. In the complex salt, however, the E_1 term due to the charge-transfer interaction between neutral and cation-radical phenothiazines was estimated to be $-38.0\ \text{kJ mol}^{-1}$ by the use of the E_1 equation. By summing E_1 and E_2, the ground-state stabilization energy of the complex salt was $E=-46.0\ \text{kJ mol}^{-1}$. We can see that, although the stabilization due to the charge-transfer interaction between phenothiazine cation radicals decreases, the total stabilization energy of the complex salt greatly increases in comparison with that of the simple salt. The reason for this is that the interaction between neutral and cation-radical phenothiazines plays an important role in the complex salt.

Since every ion radical salt belongs to a kind of ionic crystals, Madelung energy is the most important factor for the cohesive energy.[11] However, the ground-state energy stabilization due to the charge-transfer interactions between ion-radical molecules and between neutral and ion-radical molecules will be the next important factor for the total cohesive energy in crystalline ion radical salts.

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