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Phase Transition and Electronic States of Solid Ion Radical Salts

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Such crystalline ion radical salts as Würster's Blue perchlorate and K^+ *p*-Chloranil$^{\overline{\cdot}}$ are known to undergo phase transitions in the solid state. There are distinct differences in their optical and magnetic properties between the low- and high-temperature phases. Using Hubbard Hamiltonian, the electronic states of the high-temperature phases of those solid ion radical salts were explained in terms of an infinite non-alternant linear chain model, while those of the low-temperature phases, in terms of a dimer model.

The prominent magnetic, electrical and optical properties of a number of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past fifteen years.[1–17] In such 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.[11–13] There have been known several crystalline ion radical salts that undergo solid-state phase transitions. For example, a stable cation radical salt of Würster's Blue (*N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine) perchlorate undergoes a phase transition at 186 K,[1–3] while an anion radical salt of K^+ *p*-Chloranil$^{\overline{\cdot}}$, around 210—260 K.[4,8,9] In both of these salts, because of the structural change in the phase transition, the optical and magnetic properties of the high-temperature phases differ distinctly from those of the low-temperature phases.[1–10]

In previous papers,[14–17] we applied half-filled Hubbard model to the segregated stack of ion radical molecules and investigated the optical and magnetic properties of a number of crystalline ion radical salts. In the present paper, we shall apply this method to Würster's Blue perchlorate and K^+ *p*-Chloranil$^{\overline{\cdot}}$ crystals and explain the electronic states and the optical and magnetic properties of their high- and low-temperature phases. This kind of approach will be very important to investigate the mechanism of the phase transitions of those ion radical salts.

Würster's Blue Perchlorate

At room temperature the crystal is known to be orthorhombic and to be built up from non-alternant one-dimensional columns composed of equivalent Würster's Blue cation radicals along the a-axis, the intermolecular spacing between nearest neighbor cation radicals being 3.550 Å.[11] A phase change into the monoclinic form occurs at 186 K, and in the monoclinic phase the a- and c-axes are almost doubled in length in comparison with the orthorhombic modification.[11]

The magnetic susceptibility of Würster's Blue perchlorate and its temperature dependence were measured by Duffy and by Okumura.[1,2] In the region above the transition temperature, the salt had been considered to be a normal paramagnet. The paramagnetic susceptibility above the transition temperature has been reported to be consistent with a Curie-Weiss law with a Curie constant $C=0.325$ emu deg/mol and a Curie temperature $\theta=-23\pm5$ K.[2] However, the observed paramagnetism is often short of the expected 100% free radical value. For example, Duffy found it to be 94%, and Okumura, as low as 81%.[1,2] The reason for this is that, although the cation radicals have almost free spins, there may act weak antiferromagnetic exchange interaction between the cation radicals. Soos and Hughes considered the salt of the high-temperature phase to be non-alternant one-dimensional antiferromagnet with exchange interaction $2J\sum_i S_i\cdot S_{i+1}$, ($S=1/2$).[10] They used their pseudo-spin method to derive theoretical magnetic susceptibility *versus* temperature curve. The pseudo-spin result with $J=70\ \mathrm{cm}^{-1}$ gave excellent agreement between the observed and theoretical magnetic susceptibility curves in the high-temperature phase.

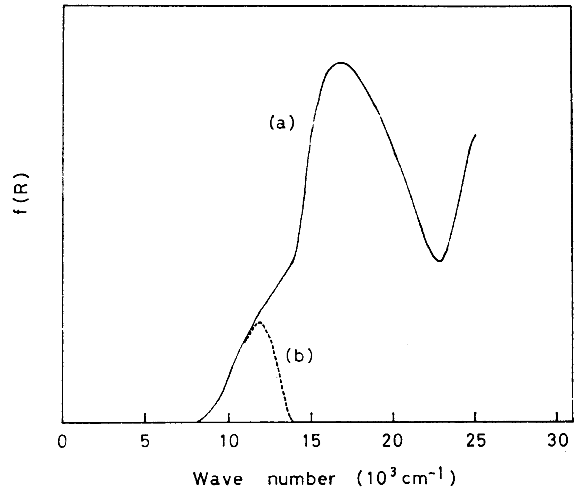

Fig. 1. (a) The observed diffuse reflection spectrum of solid Würster's Blue perchlorate salt at room temperature. The value of Kubelka-Munk function, $f(R)=(1-R)^2/2R$, was plotted *versus* wave number. (b) The intermolecular charge-transfer band of the salt. It was obtained by subtraction of the monomer absorption of the cation radical. See text and Ref. 5.

Earlier, we measured the electronic spectrum of Würster's Blue perchlorate crystal at room temperature (*i.e.*, the high-temperature phase) by means of diffuse reflection method.[5] The observed spectrum is reproduced in Curve (a) of Fig. 1, where we note a strong absorption at $16700\ \mathrm{cm}^{-1}$ and a weak shoulder around $12000\ \mathrm{cm}^{-1}$. The strong absorption at 16700 cm^{-1} corresponds well to the $16400\ \mathrm{cm}^{-1}$ band of the monomer spectrum of Würster's Blue cation radical, while the shoulder around 12000 cm^{-1} was assigned to the charge-transfer transition between the cation radicals in the solid state.[5-7,9] By subtracting the 16700 cm^{-1} monomer absorption from the observed solid-state spectrum, the intermolecular charge-transfer band of the high-temperature phase is given by Curve (b) of Fig. 1, and its peak position appears to be at 11900 cm^{-1}.

In order to understand those optical and magnetic properties of the high-temperature phase of Würster's Blue perchlorate crystal, we consider the system of non-alternant one-dimensional stack of Würster's Blue cation radicals in terms of Hubbard Hamiltonian, which can be written by[14,16]

$$\mathscr{H} = \sum_{i,j,\sigma} T_{ij} C_{i\sigma}^{+} C_{j\sigma} + I \sum_{i} n_{i\uparrow} n_{i\downarrow}, \tag{1}$$

where $n_{i\sigma} = C_{i\sigma}^{+} C_{i\sigma}$, and $C_{i\sigma}^{+}$ and $C_{i\sigma}$ are the creation and annihilation operators of an electron with σ-spin at the i-th site, respectively, and where $T_{ij}(<0)$ is the transfer matrix element between the i-th and j-th sites. The Coulomb repulsion potential, I, appears only when two electrons with up and down spins are at the same site. For non-alternant one-dimensional column of ion radicals, we consider the half-occupied molecular orbital of the unpaired electron as one site of ion radical molecule, and only take into account the transfer matrix element between the nearest neighbor sites. Hereafter, it is simply denoted by T (<0). We consider a paramagnetic state for our system, and further assume a δ-function for each elementary transition in which the spin and the wave vector of an electron are conserved. The intermolecular charge-transfer absorption of this system, $\sigma(\omega)$, is then given by[14]

$$\sigma(\omega) \propto \frac{e^2}{4} \frac{I^2}{\omega^2 \sqrt{\omega^2 - I^2}} \sqrt{4T^2 - \omega^2 + I^2}. \tag{2}$$

A schematic representation of the absorption line shape has been given in Fig. 1 of Ref. 14. The theoretical charge-transfer absorption has a sharp divergent peak at $\omega = I$, and has a band width of $\sqrt{I^2 + 4T^2} - I$ in the region of $\omega > I$. On the other hand, we examine the magnetic properties of the same system. In a region of small $|T|$ limit, the Hubbard model leads to a stabilization of the antiferromagnetic state between ion radical molecules.[16,17] For a pair of nearest neighbor ion radicals, if the small direct exchange is neglected, the energy gap between the parallel and antiparallel spin states is given by $2J = 4T^2/I$. Therefore, we can well consider our solid Würster's Blue perchlorate salt as one-dimensional antiferromagnet with an exchange interaction, J. In this respect, Soos and Hughes' treatment of regular one-dimensional antiferromagnetic model is quite adequate. Therefore, if we combine the experimental data on the peak energy of the observed charge-transfer absorption and the exchange interaction parameter derived from the magnetic susceptibility measurement, we can uniquely determine the magnitudes of I and T of Eq. 1 for our system.

We apply this approach to the high-temperature phase of the Würster's Blue perchlorate crystal. The observed peak energy of the charge-transfer absorption, 11900 cm^{-1}, thus corresponds to $I = 11900$ cm^{-1}. As for the magnitude of the transfer matrix element, by putting the estimated $I = 11900$ cm^{-1} and $J = 70$ cm^{-1} values into $J = 2T^2/I$, we obtain $T = -650$ cm^{-1} for the one-dimensional system of the Würster's Blue perchlorate salt. The $|T|$ value thus estimated is found to be much smaller than the $|T|$ values estimated with a number of other ion radical salts,[14-17] indicating weak intermolecular interaction between the Würster's Blue cation radicals.[18] This is supported by the fact that the intermolecular distance between the cation radicals in the perchlorate salt is as large as 3.550 Å and also by the spectroscopic features that the 16700 cm^{-1} band of the solid salt corresponds well to the monomer spectrum of the Würster's Blue cation radical and that the intermolecular charge-transfer band appears very weakly as a shoulder in the solid-state spectrum.

Next, we consider the low-temperature phase of the same salt. As the phase transition occurs, the non-alternant one-dimensional stack of Würster's Blue cation radicals alternates strongly in the low-temperature phase.[11] The Würster's Blue cation radicals stack predominantly in a pair-by-pair manner, so that the crystal system can be practically confined to a dimer of the cation radicals. In fact, Thomas *et al.* observed the triplet-state fine structures in the ESR spectrum below the transition temperature and determined the energy gap between the ground singlet state and the excited triplet state to be 246 cm^{-1}.[3] On the other hand, Sakata *et al.* and Ishii *et al.* measured the crystal electronic spectrum of the perchlorate salt below the transition temperature.[6,9] With decreasing temperature, they found marked increase in intensity of the low-energy charge-transfer absorption, whose peak position was at 12100±400 cm^{-1}. This absorption was assigned to the charge-transfer transition between the Würster's Blue cation radicals in the dimer.

On the basis of these experimental results, we consider the electronic state of the low-temperature phase of the Würster's Blue perchlorate salt in terms of a dimer model of Hubbard Hamiltonian, which can be written by[16]

$$\mathscr{H} = \sum_{\sigma} T(C_{1\sigma}^{+} C_{2\sigma} + C_{2\sigma}^{+} C_{1\sigma}) + I(n_{1\uparrow} n_{1\downarrow} + n_{2\uparrow} n_{2\downarrow}), \tag{3}$$

where the notations are common to those in Eq. 1. The suffixes, 1 and 2, denote two sites of ion radicals in a dimer, and $T(<0)$ is the transfer matrix element between ion radicals in the dimer. If we only take the half-occupied molecular orbital of ion radical for each site, there are six bases of the wave functions for the dimer. After solving the eigenvalue problem, we have three singlet states and one triplet state. A detail of the wave functions and the energy levels was described in a previous paper.[16] The energy of the charge-transfer absorption, $h\nu_{\mathrm{CT}}$, and the singlet-triplet energy separation, δ, are given by

$$h\nu_{\mathrm{CT}} = \left\{ \left(\frac{1}{2} I \right)^2 + (2T)^2 \right\}^{1/2} + \frac{1}{2} I, \tag{4}$$

$$\delta = \left\{ \left(\frac{1}{2} I \right)^2 + (2T)^2 \right\}^{1/2} - \frac{1}{2} I. \tag{5}$$

This dimer model was then applied to the above experimental results of the low-temperature phase of the Würster's Blue perchlorate salt. By putting the observed values of $h\nu_{\mathrm{CT}}=12100\pm400\ \mathrm{cm}^{-1}$ and $\delta=246\ \mathrm{cm}^{-1}$ into Eqs. 4 and 5, we obtain $I=h\nu_{\mathrm{CT}}-\delta=11900\pm400\ \mathrm{cm}^{-1}$ and $T=-865\pm15\ \mathrm{cm}^{-1}$, respectively. The I value thus estimated almost coincides with the $I=11900\ \mathrm{cm}^{-1}$ value of the high-temperature phase, while the $|T|$ value of the dimer is found to be appreciably larger than the $|T|=650\ \mathrm{cm}^{-1}$ value of the high-temperature phase. In view of these results, the 186 K phase transition associated with slight crystal structure modification scarcely changes the magnitude of Coulomb repulsion energy, but increases significantly the magnitude of transfer matrix element of the dimer in the low-temperature phase.

K^+ *p*-Chloranil$^{\bar{\cdot}}$

At room temperature, although there are several polymorphs, in the structure of the orthorhombic α-form the *p*-chloranil anion radicals are stacked with equal intervals, forming non-alternant one-dimensional columns parallel to the c-axis, the interplanar spacing being 3.47 Å.[12] The optical and magnetic properties and the electronic state of the room-temperature (high-temperature) phase of the K^+ *p*-Chloranil$^{\bar{\cdot}}$ salt have been already discussed in a previous paper.[16] The Hubbard Hamiltonian of Eq. 1 was applied to the non-alternant one-dimensional column of the *p*-chloranil anion radicals, and the values of $I=11800\ \mathrm{cm}^{-1}$ and $T=-820\ \mathrm{cm}^{-1}$ were obtained.

As temperature is lowered, the K^+ *p*-Chloranil$^{\bar{\cdot}}$ salt undergoes a phase transition at 210 K.[4] With increasing temperature, however, a large hysteresis occurs and the low-temperature phase changes into the high-temperature phase around 260 K. The magnetic susceptibility and its temperature dependence in the low-temperature phase were measured by Andre *et al.* and were well explained in terms of an equilibrium between ground singlet state and excited triplet state lying $\delta=400\ \mathrm{cm}^{-1}$ above the singlet state.[4] In the low-temperature phase, although there have been no crystal structure data, the magnetic behavior strongly suggests a dimeric structure of the *p*-chloranil anion radicals. The electronic spectrum of the solid salt below the transition temperature was measured by Hiroma and Kuroda.[8] With decreasing temperature, they found marked increase in intensity of the low-energy charge-transfer absorption, whose peak position was reported to be at $11500\ \mathrm{cm}^{-1}$. This absorption was assigned to the charge-transfer transition in the dimer. In order to explain those optical and magnetic properties, the dimer model of Hubbard Hamiltonian of Eq. 3 was again applied. By taking the same procedure as described in the preceding section, together with Eqs. 4 and 5, the values of $I=11100\ \mathrm{cm}^{-1}$ and $T=-1070\ \mathrm{cm}^{-1}$ were estimated for the low-temperature phase of the K^+ *p*-Chloranil$^{\bar{\cdot}}$ salt. We can also see that the $|T|$ value of the low-temperature phase is larger than the $|T|$ value of the high-temperature phase. The phase change causes a slight decrease of the I value in the low-temperature phase.

Concluding Remarks

In both of the Würster's Blue perchlorate and K^+ *p*-Chloranil$^{\bar{\cdot}}$ crystals, the high-temperature phases correspond to non-alternant one-dimensional stacks of ion radical molecules, while the phase transitions cause alternate stacks of ion radicals in the low-temperature phases. In the present paper, we cannot explain the detailed mechanism of these phase transitions, but can understand the electronic states of both high- and low-temperature phases in terms of Hubbard Hamiltonian. The motive force of the phase changes probably comes from Peierls instability in one-dimensional system of segregated stacks of ion radical molecules.

As for the transfer matrix element of the high-temperature phase, the $|T|$ value of Würster's Blue perchlorate is found to be smaller than that of K^+ *p*-Chloranil$^{\bar{\cdot}}$. In this respect, the intermolecular interaction between Würster's Blue cation radicals appears to be weaker than that between *p*-chloranil anion radicals. We can understand this difference, because the intermolecular distance between Würster's Blue cations, 3.550 Å, is longer than that between *p*-chloranil anion radicals, 3.47 Å.

In the low-temperature phases, alternate stacks of ion radical molecules cause shorter intermolecular distance in a dimer and longer distance between dimers, compared to the intermolecular distance in non-alternant stacks. On this basis, it is reasonable that, in both of the Würster's Blue perchlorate and K^+ *p*-Chloranil$^{\bar{\cdot}}$ salts, the $|T|$ values estimated with the low-temperature phases are appreciably larger than those of the high-temperature phases. Concerning the magnitude of the $|T|$ values in the low-temperature phases, the $|T|$ value of K^+ *p*-Chloranil$^{\bar{\cdot}}$ is larger than that of Würster's Blue perchlorate, so that the singlet-triplet energy separation of the former salt is wider than that of the latter. Although we have no structural information, the *p*-chloranil anion radicals may stack in the dimer more closely than do the Würster's Blue cation radicals.

The theoretical consideration made in the present paper will be useful to investigate the mechanism of the phase transitions of those solid ion radical salts.

References

1) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

2) K. Okumura, *J. Phys. Soc. Jpn.*, **18**, 69 (1963).

3) D. D. Thomas, H. Keller, and H. M. McConnell, *J. Chem. Phys.*, **39**, 2321 (1963).

4) J. J. Andre, J. Clementz, R. Jesser, and G. Weill, *C. R. Acad. Sci., Ser. B*, **266**, 1057 (1968).

5) Y. Iida and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **41**, 2615 (1968).

6) T. Sakata and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **42**, 1497 (1969).

7) J. Tanaka and M. Mizuno, *Bull. Chem. Soc. Jpn.*, **42**, 1841 (1969).

8) S. Hiroma and H. Kuroda, *Bull. Chem. Soc. Jpn.*, **46**, 3645 (1973).

9) K. Ishii, K. Kaneko, and H. Kuroda, *Bull. Chem.*

Soc. Jpn., **49**, 2077 (1976).

10) Z. G. Soos and R. C. Hughes, *J. Chem. Phys.*, **46**, 253 (1967).

11) J. L. DeBoer and Aafje Vos, *Acta Crystallogr.*, *Sect. B*, **28**, 835, 839 (1972).

12) M. Konno, H. Kobayashi, F. Marumo, and Y. Saito, *Bull. Chem. Soc. Jpn.*, **46**, 1987 (1973).

13) J. Tanaka, M. Tanaka, T. Kawai, T. Takabe, and O. Maki, *Bull. Chem. Soc. Jpn.*, **49**, 2358 (1976), and the references cited therein.

14) Y. Iida, *Bull. Chem. Soc. Jpn.*, **50**, 1445 (1977), and the references cited therein.

15) Y. Iida, *Bull. Chem. Soc. Jpn.*, **50**, 2481 (1977); **51**, 631 (1978).

16) Y. Iida, *Bull. Chem. Soc. Jpn.*, **51**, 2523 (1978).

17) Y. Iida, *Bull. Chem. Soc. Jpn.*, **51**, 3637 (1978).

18) J. Tanaka, M. Inoue, M. Mizuno, and K. Horai, *Bull. Chem. Soc. Jpn.*, **43**, 1998 (1970). In this paper, they discussed the interaction parameter between the ground and charge-transfer configurations in terms of dimer model of Würster's Blue cation radicals. Although their dimer model was not applied directly to the high-temperature phase of Würster's Blue perchlorate, they estimated the magnitude of the interaction parameter as 645 cm^{-1}, which should approximately correspond to $2|T|$ of our Hubbard model. Their value is somewhat smaller than the 1300 cm^{-1} value derived from our one-dimensional Hubbard model, thus giving a J value much smaller than the observed $J=70\ \mathrm{cm}^{-1}$.