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Spectroscopic Behavior of Würster's Blue Perchlorate and *N*-Ethylphenazyl Crystals

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The electronic absorption spectra of Würster's Blue perchlorate and *N*-ethylphenazyl in solid were measured at various temperatures ranging from 48°K to 300°K. In both cases, strong bands due to the charge-transfer between the half occupied orbitals of respective component radicals were observed in near infrared region. This assignment of these bands was supported by the polarized absorption measurement carried out with the Würster's blue perchlorate single crystal. The charge-transfer band of solid Würster's blue perchlorate was found to increase its intensity with decreasing temperatures; in particular, the increasing tendency became predominant below the phase transition point (186°K). The similar tendency was also observed for solid *N*-ethylphenazyl. The temperature dependence of the band was found to be closely related with the population of triplet excitons determined from the measurement of magnetic susceptibility or paramagnetic resonance. The separation J between the ground singlet state and the thermally accessible triplet state was determined from the analysis of the temperature dependence of the charge-transfer band to be 235 cm^{-1} and 320 cm^{-1} for Würster's blue perchlorate and *N*-ethylphenazyl, respectively.

The electronic absorption spectra of Würster's blue perchlorate (WBP) and *N*-ethylphenazyl (EP) have been studied extensively with their solutions.[1-3] In solution the spectra due to the monomers were observed at room temperature, but at low temperature new bands characteristic of the dimers were found in the near infrared region. Hausser and Murrell[2] interpreted them as the charge-transfer band between the half occupied orbitals of component radicals. From temperature and concentration dependencies of electronic absorption spectra, the enthalpy change due to the dimer formation was determined by Ooshika *et al.*[1] and by Hausser[3] to be about 5—8 kcal/mol and 2 kcal/mol for WBP and EP, respectively.

Hausser measured the static magnetic susceptibility of solid EP at three temperatures and found that the value becomes lower with decreasing

1) K. Uemura, S. Nakayama, Y. Seo, K. Suzuki and Y. Ooshika, This Bulletin, **39**, 1348 (1966); A. Kawamori, A. Honda, N. Joo, K. Suzuki and Y. Ooshika, *J. Chem. Phys.*, **44**, 4363 (1966).

2) K. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).

3) K. H. Hausser, *Z. Naturforsch.*, **11a**, 20 (1956).

temperatures.[2,3]

The paramagnetic resonance of the single crystal of WBP has been studed by McConnel *et al.*[4] They found the paramagnetic resonance signal due to triplet excitons for the WBP crystal below the orthorhombic (room temperature form) - monoclinic (low temperature form) phase transition point at 186°K. Furthermore, the sudden decrease in paramagnetic susceptibility was observed by several authors[5] with WBP at this point. These facts show that the cations form dimers in the WBP crystal of the low temperature (monoclinic) form resulting in the ground singlet state and the excited triplet state.[4] These two states may be thought to be brought about by the exchange interaction between the two cations in the monoclinic crystal. The singlet-triplet separation J was estimated to be 246 ± 20 cm^{-1} by McConnell *et al.* from the temperature dependence of ESR intensity.[4]

Under these circumstances, we have undertaken to study in detail the optical properties of the WBP and EP crystals at various temperatures in addition to their magnetic properties. One of our main purpose is to clarify the existence of the triplet exciton from electronic absorption measurements at various temperatures ranging from 50°K to 300°K.

Experimental

WBP and EP were prepared and purified by the same methods as described in Refs. 6 and 7, respectively. The purified sample of EP was kept at −70°C because it was fragile at room temperature.

A Cary recording spectrophotometer model 14 M was used for the measurements of electronic absorption spectra of solutions and solid samples. The solid films for absorption measurements were prepared by coating powdered samples on quartz plates by a stainless steel spatula. The solid samples prepared in this way were shown to be suitable for the measurements of absorption spectra in the near infrared and visible regions. The reliability of this method was checked by comparing the spectra of solid thin films with those observed with single crystals by the aid of a microspectrophotometer. For example, the electronic absorption spectra of tetracyanobenzene and of the naphthalene-tetracyanobenzene complex observed by the present method agree well with those observed with the respective single crystals.[8] Absorption measurements at low temperatures were made by using ordinary glass Dewar vessels containing liquid helium or liquid nitrogen as refrigerant.

A spectrophotometer attached with a microscope and a Roschen type polarizer[9] was used for the polarized absorption measurement of a single crystal.

ESR spectra were measured with a Hitachi X band spectrometer with 100kc field modulation.

Results and Discussion

Polarized Absorption Spectra of WBP. The electronic absorption spectra of the solid WBP measured at various temperatures are shown in Fig. 1. In this figure, the spectra of the ethanol solution of WBP measured at various temperatures are also shown for the purpose of comparison. Figure 1 shows that the absorption spectra of the solution and solid samples at room temperature are similar to each other[10] except for the fact that the latter exhibits a weak absorption in the near

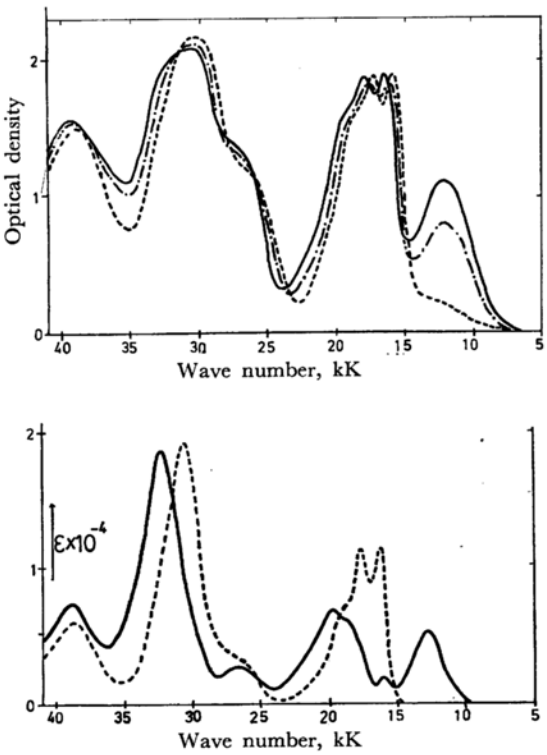


Fig. 1. Absorption spectra of WBP ($((CH_3)_2N\text{-}\bigcirc\!\!\oplus\!\!\text{-}N(CH_3)_2\cdot ClO_4^-$) at various temperatures.
upper part; in solid, —— 48°K, - - - 100°K, ---- 300°K
lower part; in ethanol solution, —— 110°K, ---- 295°K

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

5a) K. Okumura, *J. Phys. Soc. Japan*, **18**, 69 (1963). b) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

6) L. Michaelis and S. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).

7) H. MacIlwain, *J. Chem. Soc.*, **1937**, 1710.

8) In the ultraviolet region, the scattering of incident light was found to give some effect to the observed intensity, although the observed peak wavelengths were correct.

9) J. Tanaka, This Bulletin, **36**, 833 (1963).

10) The absorption bands in solid show the red shift of about 700 cm^{-1} compared with the corresponding bands of the solution.

infrared region longer than 700 mμ. This weak band observed for the solid sample is intensified with decreasing temperatures and its maximum wavelength corresponds well to the charge-transfer band of the radical dimer observed by Hausser[2,3] with the solution at low temperature. Therefore, it can be regarded as the band caused by the charge-transfer interaction between the WB cations in crystal.

In order to give an additional support to this interpretation, we measured the polarized absorption spectrum of the single crystal of WBP at room temperature. The results are shown in Fig. 2. The actual measurements were made by light polarized parallel to the a′ and c′ direction of the crystal shown in Fig. 3. The used crystal is a flat plate and shows the straight extinction under a polarizing microscope. This means that at least one crystal axis is on the observed plane, because the room temperature form of WBP is orthorhombic.[4] Furthermore, from the X-ray diffraction experiment,

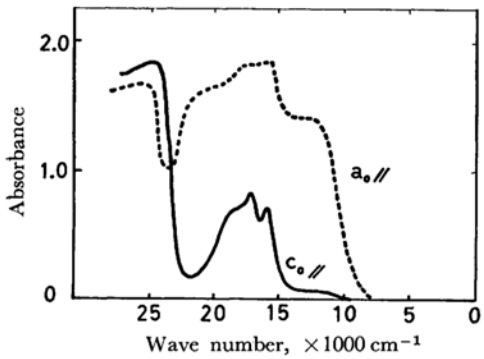


Fig. 2. Polarized absorption spectrum of the single crystal of WBP at room temperature.

the a′ c′ plane was determined to be the a_0c_0 plane.*1. On the basis of the crystal structure shown in Fig. 3, let us consider the polarization of the band near 600 mμ which can be assigned to the $^2B_{3g} \rightarrow {}^2B_{1u}$ transition of the free radical cation whose transition moment is parallel with its long molecular axis connecting the two nitrogen atoms.[11,12] This band can be expected to split into the two components parallel to a_0 and c_0 axes with the intensity ratio of $I_{//a_0} : I_{//c_0} = [\tan(90°-37.5°)]^2 : 1 = 1.7 : 1$, in the approximation of the oriented gas model. According to our measurement, this band has the maximum and minimum intensities in the directions parallel to the a′ and c′ axes, respectively, and the dichroic ratio was determined to be $I_{//a'} : I_{//c'} = 2.2 : 1$. This means that a′ and c′ axes correspond to a_0 and c_0 axes, respectively.

As is clearly seen in Fig. 2, the characteristic band which appears in the wavelength region longer than 700 mμ has the transition moment parallel to the a′ (a_0) direction. This seems to support the interpretation that the band is accompanied by the charge-transfer between the half occupied orbitals of the component radicals, in view of the fact that the line connecting their centers is parallel to a′ (a_0) axis.

Temperature Dependence of Charge-Transfer Band. *a) WBP.* In order to check the variation of the absorption spectrum above and below the phase transition point at 186°K, we measured the absorption spectrum of solid WBP at various temperatures ranging from 48°K to 300°K. The results are shown in Fig. 1. From this figure it is concluded that with lowering temperature the charge-transfer band increases its intensity and other bands due to the excitation within the radical

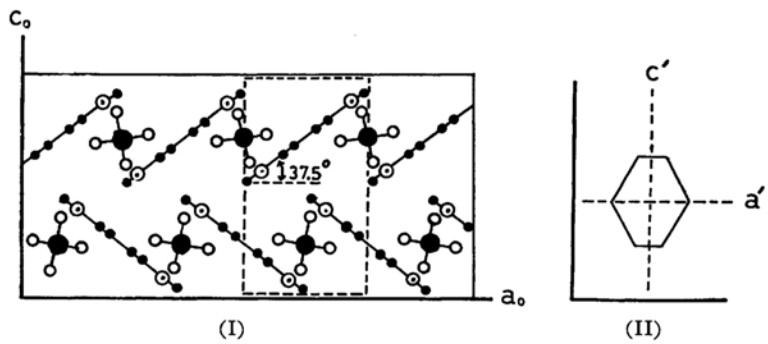


Fig. 3. I. Projection of the orthorhombic structure of WBP onto the a_0c_0 plane. ● Cl, ⊙ N, ○ O, • C
II. Rough sketch of the single crystal of WBP used for the polarized absorption spectrum measurement. a′ and c′ are extinction positions.

*1 We are indebted to Mr. Y. Oohashi of our Institute for his help in performing the X-ray diffraction experiment.

11) A. D. Albrecht and W. T. Simpson, *J. Am. Chem. Soc.*, **77**, 4461 (1955).
12) M. Goeppert-Mayer and K. J. McCallum, *Rev. Mod. Phys.*, **14**, 248 (1942).

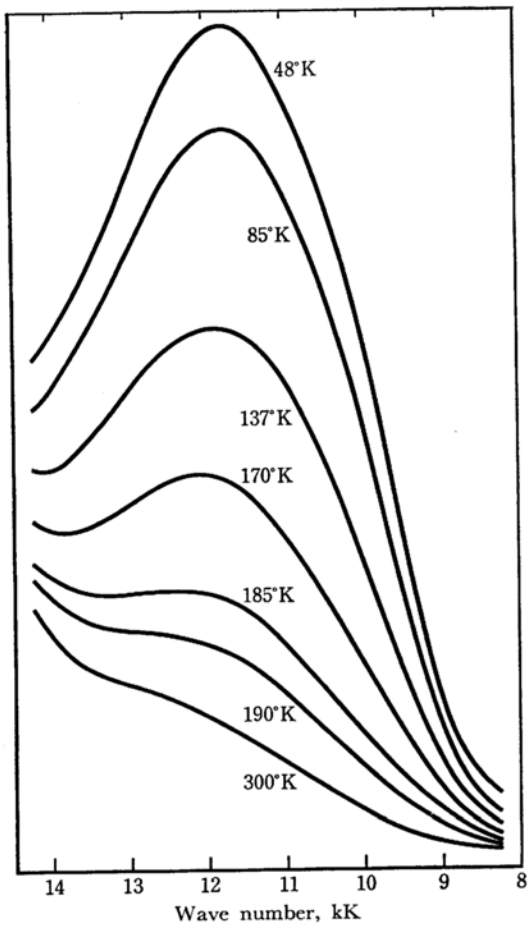


Fig. 4. The charge-transfer band of WBP at various temperatures.

cation leave their intensities almost unaltered, though their peaks shift by 700—800 cm^{-1} by changing the temperature from 300°K to 48°K.

We measured very carefully and precisely the temperature dependence of the intensity of the charge-transfer band, with the result shown in Fig. 4. This figure clearly shows that the intensity increase becomes suddenly remarkable below phase transition point. Since the dimer may be the unit in the WBP crystal below the phase transition point,[4] the observed sudden increase in absorption intensity may be thought to be due to the radical dimer formation. The details of this point are discussed in the later part in comparison with the temperature dependence of the magnetic properties.

The charge-transfer band of the WBP crystal shifts to longer wavelengths by about 1000 cm^{-1} than that of the dimer in solution. The same tendency was observed for EP. This shift may be explained qualitatively by considering the interaction between the induced transition dipoles of adjacent dimers.

b) EP. The electronic absorption spectra of EP in ethanol-ether solution and in solid are shown in Fig. 5. Concerning the solution spectrum, there appears no absorption in the near infrared region at room temperature, but at low temperature a charge-transfer band due to the dimer appears at 800 mμ.[3] The spectrum of solid EP well coincides as a whole with that of dimer in solution, although the charge-transfer band in the former appears at 900 mμ and therefore shifts by 1600cm^{-1} to lower frequencies compared with that in the latter.

The absorption spectrum of solid EP was measured at various temperatures ranging from 300°K to 55°K with the result shown in Fig. 6. The charge-transfer band of solid EP greatly increases its intensity with lowering temperature and this intensity increment becomes saturated at about 50°K. This temperature dependency is similar

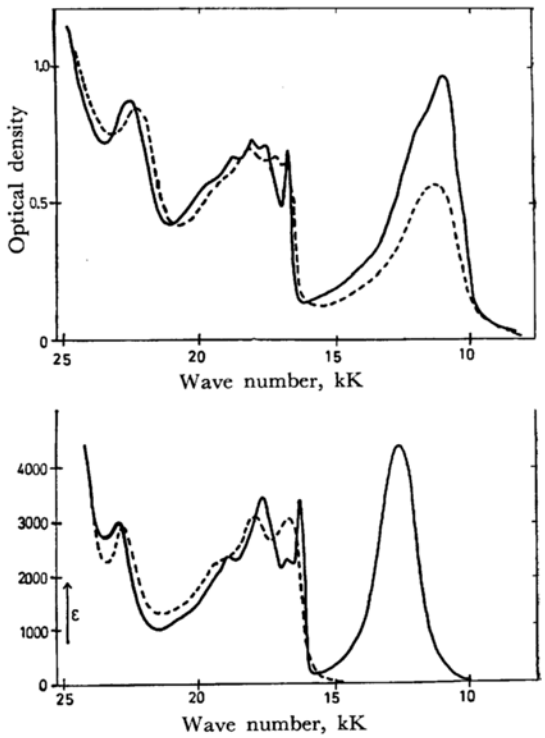
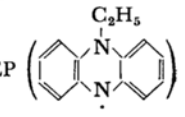


Fig. 5. Absorption spectra of EP 

at low and high temperatures.
upper part; in solid, —— 50°K, ---- 275°K
lower part; in ethanol(2)-ether(1) solution,
—— 110°K, - - - 295°K

13) As is clearly seen in Figs. 5 and 6, the charge-transfer band is composed of two peaks in the solid sample of EP, while the solution spectrum shows only one peak. This splitting may be due to either Davydov splitting or vibrational structure.

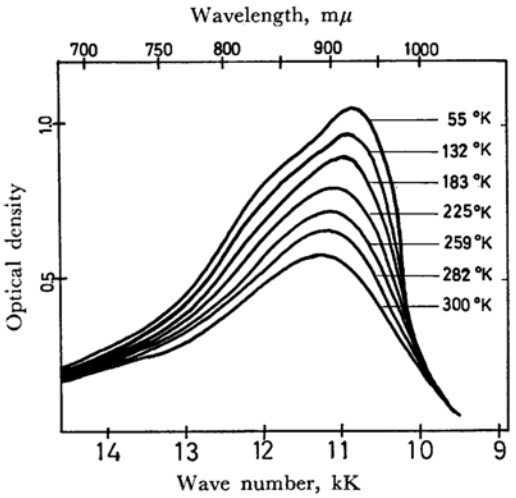


Fig. 6. The charge-transfer band of EP at various temperatures.

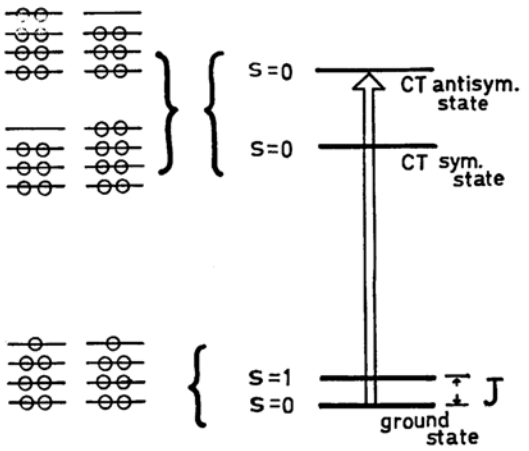


Fig. 7. Energy diagram and configurations of a radical dimer.

to that observed for the low temperature form of WBP crystal. This suggests that dimers are the unit in the EP crystal as well as in the WBP crystal below the phase transition point.[14]

The Relation Between the Temperature Dependence of Charge-Transfer Band and Magnetism. Now let us consider the reason why the charge-transfer band increases remarkably its intensity with the decreasing temperature for the WBP crystal below the phase transition point and for the EP crystal. This anomalous phenommenon can be explained by considering the existence of the thermally accessible triplet excitons in these crystals.

As described above, the radical dimer may be considered to be the unit of the structure in these crystals.[15] In the radical dimer a singlet state and a triplet state may be caused as the result of the exchange interaction between the two radical monomers of the doublet state. In the cases of WBP and EP the singlet state may conceivably be lower than the triplet state; that is to say, the ground state is singlet and the triplet excited state exists above it with the energy separation J whose magnitude is of the same order as the thermal energy kT.

The singlet triplet separation J may be considered, as in general, to be originated from the exchange interaction between two unpaired electrons in the half occupied orbitals of the component radicals. Furthermore, above the triplet state of the radical dimer, there exists the charge-transfer state which corresponds to the electron transfer between the half occupied orbitals of the component radicals. The energy diagram of this dimer is schematically shown in Fig. 7. The dimer is assumed to have a center of symmetry, as is thought to be the case in WBP and EP. When the dimer has a center of symmetry, there are two charge-transfer states, a symmetric one and an antisymmetric one; the latter is higher than the former[2] and the transition from the ground singlet state to the latter is allowed for the sandwich type dimer.

Since the charge-transfer band is observed in the near infrared region for both WBP and EP, the energy separation between the charge-transfer state and the singlet ground state may be considered to be small. From this it may be inferred that the mixing of these two states stabilizes the singlet ground state and contributes to some extent to the singlet triplet separation J.[16] However, from an analogy with the case of the hydrogen molecule the main contribution to J might be considered to be still the exchange interaction between the two unpaired electrons.[17]

On the basis of the energy level diagram shown in Fig. 7, we consider the mechanism of the temperature dependence of the absorption intensity. When a dimer is in the ground singlet state, the transition to the antisymmetric charge-transfer state is allowed, but when a dimer is in a thermally accessible triplet state the transition is forbidden from the spin multiplicity. Furthermore, as is clear from the electron configuration shown in Fig. 7, the corresponding charge-transfer triplet state does not exist. Therefore the intensity of the charge-transfer band may be considered to be propor-

14) The EP crystal has no phase transition between room temperature and 50°K.

15) The situation is the same for the solid samples with which the temperature dependence of the absorption intensity was actually measured, because they are composed of the micro crystals.

16) H. M. McConnell, "Molecular Biophysics," ed. by B. Pullman and M. Weissbluth, Academic Press, New York (1965), p. 311.

17) The authors would like to express their sincere thanks to Professor R. S. Mulliken for his valuable suggestion on this point.

tional to the number of dimers in the ground singlet state. Neglecting the interaction between dimers, the populations of the ground singlet and excited triplet states may be assumed to follow the Boltzmann distribution law. When J is of the order of magnitude of thermal energy kT, the intensity of the charge-transfer band may be expected to be strongly dependent on temperature and the change in the charge-transfer band intensity with temperature may be regarded as the measure of the number of dimers in the thermally accessible triplet state (see Fig. 8). When we consider the crystal which is an assembly of dimers, their excited states must be replaced by a exciton traveling among them. However, the preceding discussion may still be approximately applicable.

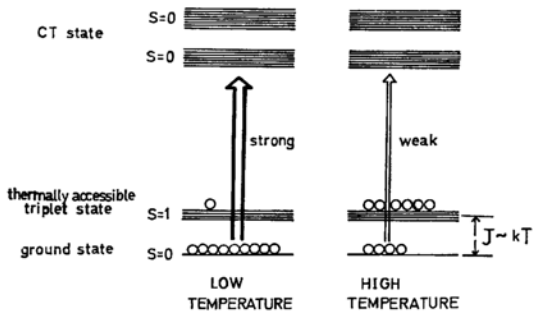


Fig. 8. A schematic explanation of the temperature dependence of charge-transfer band intensity in the solid. An arrow shows an allowed charge-transfer transition. Circles represent schematically the number of dimers of each state.

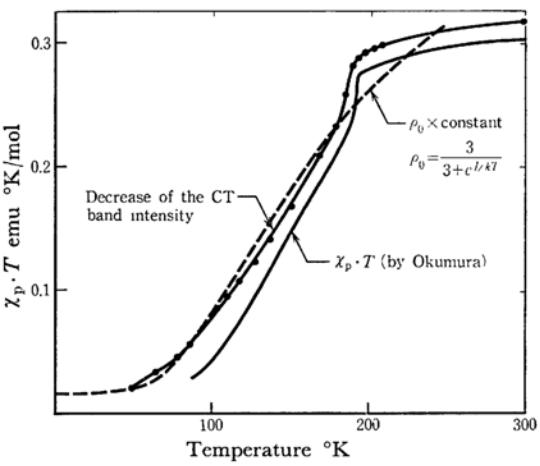


Fig. 9. Intensity of the charge-transfer band and magnetic susceptibility of WBP.

In order to make sure of the above discussion, we have undertaken to compare quantitatively the temperature dependency of the charge-transfer band intensity with that of magnetic susceptibility. The result of WBP is shown in Fig. 9. The curve showing the temperature dependence of the intensity (A) of the charge-transfer band is satisfactorily parallel with that plotting $\chi_p \cdot T$ against T measured by Okumura,[5a] where $\chi_p \cdot T$ values are known to represent the population of the dimer in the excited triplet state.[18] This means that our explanation on the temperature dependence of the charge-transfer band is correct.

The intensity of the charge-transfer band of the WBP crystal varies, though to much smaller extent than in the low temperature phase, in the room temperature phase in which WB cations are equally spaced. This seems to suggest that there exists antiferromagnetic interaction between spins on the WB cation radicals and the probability of neighboring cations having antiparallel spins decreases in higher temperatures.

Neglecting the interaction between dimers as the first approximation, the population of the triplet state ρ_0 can be represented as follows:

$$\rho_0 = 3/(3 + e^{J/kT})$$

By combining the above equation with the observed temperature dependence of the absorption intensity of the charge-transfer band, J is obtained to be $\sim 235\ \mathrm{cm}^{-1}$. This value of J agrees well with that obtained from the analysis of ESR data by McConnell ($J = 246 \pm 20\ \mathrm{cm}^{-1}$).[4]

The same consideration was applied to the solid EP and the value of J was evaluated to be $320 \pm 20\ \mathrm{cm}^{-1}$ from the temperature dependence of charge-transfer band. We also measured paramagnetic resonance spectra of the solid EP to check this value. The transition of $\Delta M = \pm 2$ was observed in addition to the ordinary transition of $\Delta M = \pm 1$.

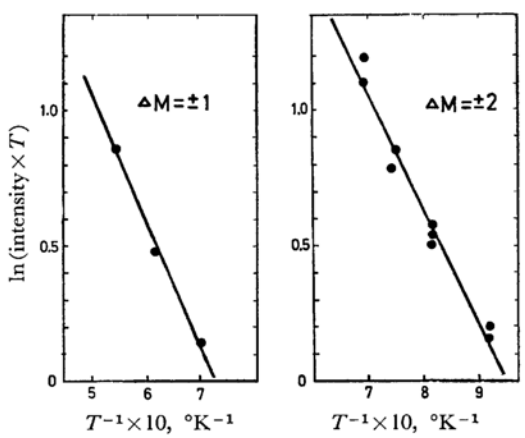


Fig. 10. Temperature dependence of paramagnetic resonance spectra of solid EP. Intensity is in arbitrary unit.

18) In connection with the above discussion, it may be added that we are not concerned with the absolute value of the population of the triplet state but only with its temperature dependence. Therefore, only the parallelism between the A-T and $\chi_p \cdot T$-T curves is important in Fig. 9. The similar parallelism can also be obtained by the use of Duffy's data[5b] instead of Okumura's data.

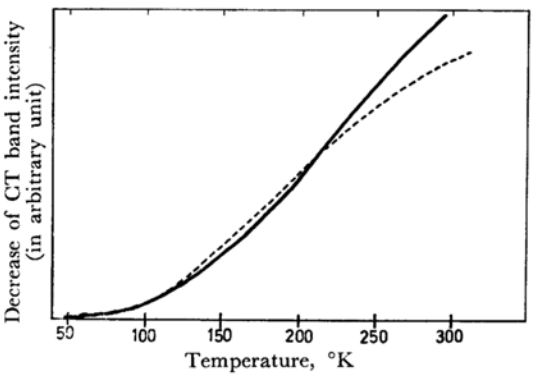


Fig. 11. Temperature dependence of the charge-transfer band intensity of solid EP. A solid line shows the decrease in the charge-transfer band intensity from the saturated value at 50°K. A dashed line represents the relation between $k\rho_0(J=320\,\mathrm{cm^{-1}})$ and T; k is a constant determined in such a way as $k\rho_0$'s fit well to the observed intensity decreases in low temperature region.

The ESR intensity I was measured at various temperatures with the results given in Fig. 10. This figure shows that a linear relationship is satisfied between $\ln IT$ and $1/T$. From the temperature dependence of paramagnetic resonance spectra, $J=330\pm20\,\mathrm{cm^{-1}}$ was obtained for $\Delta M=\pm1$, and $J=300\pm40\,\mathrm{cm^{-1}}$ for $\Delta M=\pm2$. These values agree well with the value obtained from the charge-transfer band.

As is clearly seen in Fig. 11, the experimental curve of the charge-transfer band intensity are somewhat off from the first order theoretical curve. This discrepancy becomes predominant at higher temperatures both for WBP in the low temperature phase and for EP. The reason for this discrepancy may be considered to be as follows:

1) The change in the intermolecular distance by thermal expansion.

2) The phonon induced interaction between triplet excitons.[19,20]

3) The exchange interaction between dimers.[21,22]

We also measured the temperature dependence of the other salts, especially of Würster's red perchlorate, paraphenylenediamine perchlorate and paraphenylenediamine bromide. As to these salts, such a remarkable intensity change in electronic absorption spectra as that observed with WBP and EP could not be found. This fact seems to correspond to the findings that these salts are diamagnetic at room temperature. The value of J seems to be large for these salts compared with kT.

Recently, Pott, Kommandeur *et al.*[23-26] suggested that the phase transition of WBP to be a disproportionation

$$2\ \mathrm{TMPD^+} \rightleftharpoons \mathrm{TMPD} + \mathrm{TMPD^{2+}}$$

(high temperature phase) (low temperature phase)

From our experimental results, however, this mechanism can be rejected

As is clearly seen in Fig. 1 showing the absorption spectrum of solid WBP, the 600 mμ band with vibrational structure corresponding to the $^2B_{3g}\rightarrow{}^2B_{1u}$ transition of the monopositive ion leaves its intensity and shape unaltered below the phase-transition point,[27] with the small blue shift of peak wavelengths by 700—800 $\mathrm{cm^{-1}}$ at most. This means that WB cations themselves do not suffer a large change by the phase transition and that the change in the weak interaction between WB cations is the cause of the phase transition. At least the above-mentioned observation can not be explained at all by the disproportionation mechanism by which the dipositive cation and the neutral molecule are produced below the phase-transition point.

Furthermore, the following fact may be added as a supplementary support to our opinion that the disproportionation mechanism by Pott, Kommandeur *et al.* is wrong. According to their mechanism, the singlet-triplet separation caused by the interaction between the half-occupied orbitals belonging to the neighboring WBP cations must amount to $\sim$1.5 eV (the difference between the transition energy of the charge-transfer band and the J value). This value seems to be too large judging from the distance between the two cation radicals and therefore from the magnitude of the overlap integral between the two orbitals.

The authors would like to express their sincere thanks to Professor J. Tanaka of Nagoya University for his kind advice and discussion. Their thanks are also due to Dr. H. Hasegawa and Dr. T. Maruyama of Japan Electron Optics Laboratory Co., Ltd. for the measurement of temperature dependence of the ESR signal due to $\Delta M=\pm2$ transition.

19) H. M. McConnell and Z. Soos, *J. Chem. Phys.*, **40**, 586 (1964).
20) D. B. Chesnut, *ibid.*, **41**, 472 (1964).
21) Z. G. Soos, *ibid.*, **43**, 1121 (1965).
22) Z. G. Soos, *ibid.*, **46**, 253 (1967).
23) H. J. Monkhorst and J. Kommandeur, *ibid.*, **47**, 391 (1967).
24) G. T. Pott and J. Kommandeur, *ibid.*, **47**, 395 (1967).
25) H. J. Monkhorst, G. T. Pott and J. Kommandeur, *ibid.*, **47**, 401 (1967).
26) G. T. Pott, C. F. van Bruggen and J. Kommandeur, *ibid.*, **47**, 408 (1967).
27) This finding was obtained as the repeated careful experimental works. The same conclusion was also obtained from the measurement by the KBr pellet method.