Polarized Absorption Spectra of Single Crystals of Ion Radical Salts. III. Temperature Dependence of the Crystal Spectra of Potassium-Chloranil

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The polarized absorption spectra in the 10000—37000 cm^{-1} region were observed on the single crystal of the water-free modification of the potassium-chloranil salt, $K^+ \cdot (chloranil)^-$, by using a microspectrophotomer, and the variation of the spectra with temperature was examined. The crystal gives a near-infrared absorption band associated with the charge transfer between chloranil radical anions, the maximum of which is located at 11.5×10^3 cm^{-1}. The absorption bands in the 20000—37000 cm^{-1} region were assigned to the local-excitation bands associated with the transitions in the chloranil anion. The intensity of the charge-transfer band gradually increases on lowering the temperature. An abrupt increase of intensity occurrs in the charge-transfer band at the phase-transition point. There is a close correlation between this change and the temperature dependence of the paramagnetic susceptibility of the salt.

The potassium-chloranil anion radical salt, $K^+ \cdot (chloranil)^-$, has been reported to exhibit a phase transition at about 210 K, where the salt changes from the "low susceptibility" to the "high susceptibility" form.[1-3] It was found by Andre and Weill[3] that the latter form is stabilized when the powder of K·(chloranil) is dispersed in KBr matrix, whereas the former form is stabilized when dispersed in LiF matrix, and a strong near-infrared band appears in the optical absorption spectrum of the powder dispersed in LiF pellet, but not in the spectrum of the powder dispersed in KBr pellet. They also examined the polarizations of the absorption bands of a single crystal by means of an optical system composed of a polarizing microscope and an interference filter, and confirmed that the near-infrared absorption band mentioned above is polarized in the direction of the molecular columns of chloranil anion, hence is a charge-transfer band. But, the details of the single crystal spectrum has not been reported.

The room-temperature absorption spectrum of K·(chloranil) powder has been also given by Iida[4] and by Sakai *et al.*[5]

Although these previous authors have not described the effect of water, we noticed that the K·(chloranil) salt has a tendency to take water molecules into the crystal lattice, particularly, when it is kept in the form of a crystalline powder, and there is an appreciable difference in the single-crystal spectrum between the water-free and water-containing modifications.

Recently, the crystal structure of the water-free modification at the room temperature was determined by Konno *et al.*[6] Thus, in the present study, we have investigated the polarized absorption spectrum of the single crystal of the water-free modification of K·(chloranil) and examined its temperature dependence.

Experimental

The polarized absorption spectra were measured by means of a microspectrophotometer equipped with a small cryostat at the specimen stage to keep the crystals at low temperature.[7,8] The measurement was done over the temperature range from the room temperature to 160 K.

The K·(chloranil) salt was synthesized according to the method reported by Torrey and Hunter.[9] The single crystals of microscopic size[10] for the measurement of absorption spectrum were prepared by the recrystallization either from acetone solution or from acetonitrile solution. In this case, the solvent and/or water molecules are included in the crystal to give the solvent-containing modification, but they can be easily taken out from the crystal by evacuation. In the present study, the specimen was placed in the cryostat and evacuated for a period sufficient to convert the crystals to the solvent-free state prior to the measurements of spectra, and the spectrum was observed without breaking the vacuum.

According to Konno *et al.*,[6] there are two solvent-free modifications of the K·(chloranil) salt at the room temperature, which are called the α- and β-form respectively. We examined the X-ray diffraction pattern of the evacuated powder. Although most diffraction lines were identified as those of the α-form, there were weak lines which were due to the β-form: the amount ratio of the α-form to the β-form was estimated as about 10 : 1. In carrying out the measurement with the microspectrophotometer, it was not possible to differentiate the β-form crystals from the α-form ones. We observed the spectra on several different crystals but obtained identical results. Therefore, we shall tentatively assume that the spectra discussed in the present paper are those of the α-form crystal.

Results and Discussion

Room Temperature Spectra and Assignment of Absorption Bands. According to Konno *et al.*, the α-form crystal is orthorhombic, space group $P2_12_12_1$ with unit cell dimension: $a=13.49$, $b=17.02$, $c=4.03$ Å.[6] The

1) J. J. Andre, J. Clementz, R. Jesser, and G. Weill, *C. R. Acad. Sci., Paris Ser. B*, **266**, 1057 (1968).
2) J. J. Andre and G. Weill, *ibid.*, **269**, 499 (1969).
3) J. J. Andre and G. Weill, *Chem. Phys. Lett.*, **9**, 27 (1971).
4) Y. Iida, This Bulletin, **43**, 2772 (1970).
5) N. Sakai, I. Shirotani, and S. Minomura, *ibid.*, **44**, 675 (1971).
6) M. Konno, H. Kobayashi, F. Marumo, and Y. Saito, *ibid.*, **46**, 1987 (1973).
7) H. Kuroda, T. Kunii, S. Hiroma, and H. Akamatsu, *J. Mol. Spectrosc.*, **22**, 60 (1967).
8) The cryostat was designed and constructed by Mr. K.Kaneko in our laboratory.
9) H. A. Torrey and W. Hunter, *J. Amer. Chem. Soc.*, **34**, 702 (1912).
10) The crystals used here were thin plates elongated along c-axis, (20—30 μ in length), the width in the b-axis direction being about 5 μ.

unit cell contains four formula units of K·(chloranil), and the chloranil anions are stacked face-to-face on each other to form molecular columns parallel to the c-axis.

The polarized absorption spectra were measured on the (100) face of a single crystal for the polarizations parallel to the b- and c-axes respectively. The spectra obtained at the room temperature are shown in Fig. 1. The wave number and the relative intensity of each observed peak are listed in Table 1.

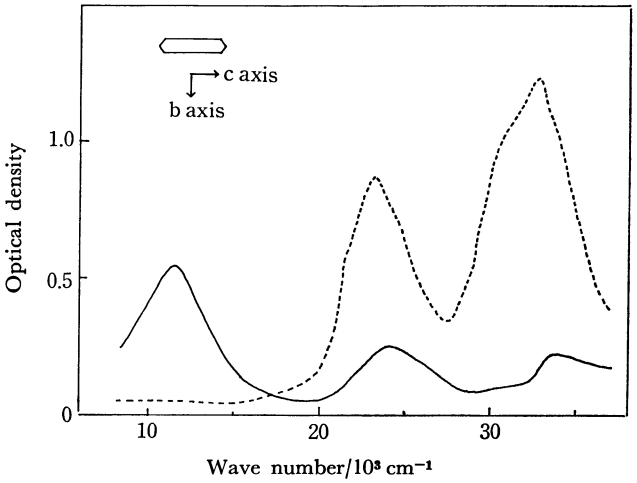

Fig. 1. Room-temperature spectra of the potassium-chloranil crystal.

(—— c-axis spectrum, ····· b-axis spectrum)

Table 1. Wave numbers and relative intensities of absorption peaks

(Intensities are given in parentheses)

	c-axis spectrum $\tilde{\nu}$ [10^3 cm^{-1}]		b-axis spectrum $\tilde{\nu}$ [10^3 cm^{-1}]	
CT-band	11.5	(0.62)		
($^2B_{1u}\leftarrow{}^2B_{2g}$)			23.1	(1.00)
($^2A_u\leftarrow{}^2B_{2g}$)	24.0	(0.28)		
($^2B_{1u}\leftarrow{}^2B_{2g}$)			30.7 32.7	(1.66)
	33.4	(0.3)		

The 11.5×10^3 cm^{-1} band is strongly polarized in the c-axis direction which is the direction of the column of the chloranil anion. In this region, we can expect no local-excitation band associated with the transition in the chloranil anion. Thus we can safely assign this band to the charge-transfer band due to the interaction between chloranil anions. Although Andre and Weill[3] reported that the charge-transfer band disappears in the "high susceptibility" form, this band is observed still with a considerable intensity in the c-axis spectrum at the room temperature.

In order to find out the interpretation for the spectra in the region above 20000 cm^{-1}, we carried out the SCF-MO-CI calculations on the transition in the free chloranil anion. We used here the method of Longuet-Higgins and Pople for the open-shell π-conjugated system.[11] The semiemprical parameters were determined by using the Nishimoto-Mataga's formula for the two-center repulsion integrals,[12] and the Nishimoto-Forster's formula[13] for the two-center resonance integrals.[14] We assumed the D_{2h} geometry for the chloranil ion, and took the bond lengths and bond angles estimated from the crystal structure data of the chloranil salt of Würster's blue.[15] In Fig. 2, the results of calculation are compared with the transitions observed in the solution spectrum of the chloranil anion. There are two types of transition, namely, $^2B_{1u}\leftarrow{}^2B_{2g}$ and $^2A_u\leftarrow{}^2B_{2g}$, the transition moments of which are respectively parallel and perpendicular to the molecular axis connecting the two oxygen atoms. Although there are some discrepancies between the calculation and observation, we can assign the absorption bands observed in the solution spectrum at 22.2×10^3 cm^{-1} (2.75 eV) and 31.1×10^3 cm^{-1} (3.86 eV) respectively to the first and second $^2B_{1u}\leftarrow{}^2B_{2g}$ transitions, and the one observed at 27.5×10^3 cm^{-1} (3.14 eV) to the first $^2A_u\leftarrow{}^2B_{2g}$ transition. On the basis of such interpretation of the solution spectrum of the chloranil anion, we examined the crystal spectrum. If we assume the oriented-gas model and estimate the dichroic ratio, I_b/I_c, of absorption band for the α-form crystal of the potassium-chloranil, we obtain 3000 for the $^2B_{1u}\leftarrow{}^2B_{2g}$ transition and 0.32 for the $^2A_u\leftarrow{}^2B_{2g}$ transition of the chloranil anion. Thus an absorption band due to a $^2B_{1u}\leftarrow{}^2B_{2g}$ transition should be almost completely polarized in the b-axis direction when the crystal spectrum is observed on the (100) face, while the one due to a $^2A_u\leftarrow{}^2B_{2g}$ transition should be stronger in the c-axis spectrum than in the b-axis spectrum.

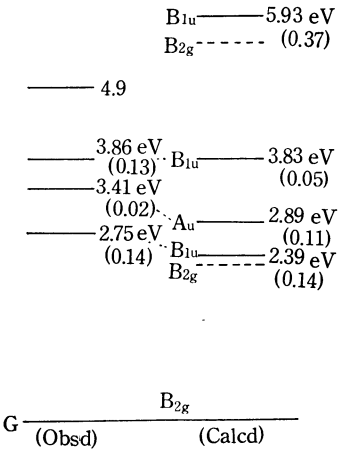

Fig. 2. Observed and calculated energy levels of the chloranil anion, (—— allowed, ····· forbidden). The oscillator strengths are given in parentheses.

11) H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc., Ser. A*, **68**, 591 (1955).

12) K. Nishimoto and M. Mataga; *Z. Phys. Chem.* (Frankfurt), **12**, 335 (1957).

13) K. Nishimoto and L. S. Forster, *Theor. Chim. Acta*, **3**, 407 (1965); **4**, 155 (1966).

14) The parameters used for chlorine atom are as follows: $-W_\mu=23.3$ eV, $\gamma_{\mu\mu}=10.79$ eV, $\beta_{C-Cl}=2.99\ r-6.00$ eV, where r is the interatomic distance.

15) J. L. de Boer and A. Vos, *Acta Crystallogr.*, **B24**, 720 (1968).

Thus the 32.7×10^3 cm^{-1} band observed in the b-axis spectrum can be assigned to the local-excitation band associated with the 31.1×10^3 cm^{-1} ($^2B_{1u}\leftarrow{}^2B_{2g}$) transition of the chloranil anion, although a weak absorption peak is observable at 33.4×10^3 cm^{-1} in the c-axis spectrum. Seemingly, the first strong absorption band in the b-axis spectrum observed at 23.1×10^3 cm^{-1} is associated with the 22.2×10^3 cm^{-1} ($^2B_{1u}\leftarrow{}^2B_{2g}$) transition of the chloranil anion. However, the dichroic ratio in this region is evidently too small. It should be noted that, in the 20000—30000 cm^{-1} region, we can expect another absorption band associated with the 27.5×10^3 cm^{-1}($^2A_u\leftarrow{}^2B_{2g}$) transition of the chloranil anion. Thus, it is likely that the 24.0×10^3 cm^{-1} band in the c-axis spectrum is not the c-axis component corresponding to the 23.1×10^3 cm^{-1} band of the b-axis spectrum, but is the one mainly due to the $^2A_u\leftarrow{}^2B_{2g}$ transition.

Temperature Dependence of the Spectra. The crystal spectra observed at several different temperatures are shown in Fig. 3. We found that a significant change appeared mainly in the region of the charge-transfer band. Only a small change was detected in the region of local-excitation bands. Above the phase-transition point, the intensity of the charge-transfer band gradually increased on lowering the temperature. An abrupt rise of intensity occurred near the phase-transition point with a decrease in the band width.

In Fig. 4, the intensity change of the charge-transfer band is compared with the change in the magnetic susceptibility.[16] Clearly there is a close correlation between them. The behavior found here is quite analogous to the one reported for the Würster's blue perchlorate. The latter has been explained with the model that the interaction between neighboring Würster's blue cation radicals gives a singlet state and a triplet state, in which the former is a little stabilized in respect to the latter, and the intensity of the charge-transfer band is governed by the singlet population in the crystal while the paramagnetism is governed by the triplet population.[17] A similar model seems to be applicable also for the K·(chloranil) salt.

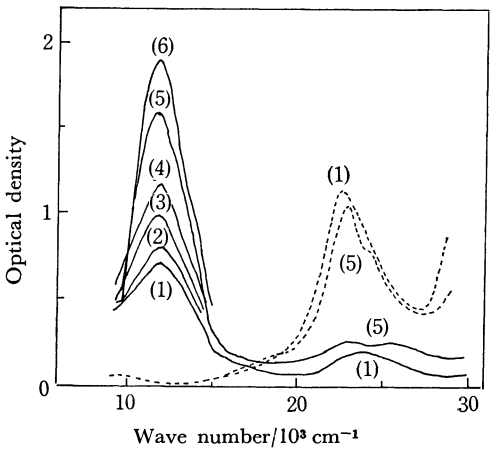

Fig. 3. Temperature dependence of the crystal spectra of the potassium-chloranil. (1): 297 K, (2): 280 K, (3): 240 K, (4): 218 K, (5): 209 K, and (6): 163 K.
(—— c-axis spectrum, ····· b-axis spectrum)

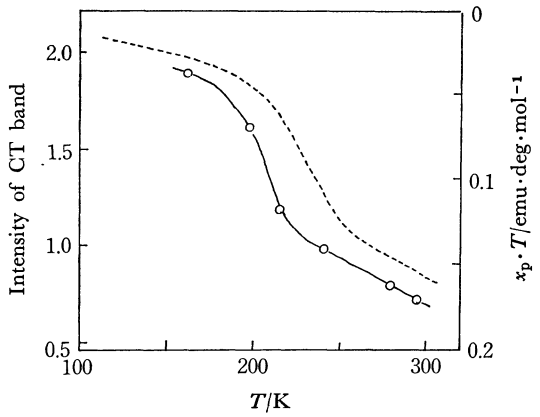

Fig. 4. Variation of the intensity of the charge-transfer band (——) and the magnetic susceptibility (·····)

In the room-temperature phase of the K·(chloranil), the chloranil anions are equally spaced in the column to give a crystal structure of monomeric form, the intermolecular spacing being 3.47 Å. The abrupt intensity increase of the charge-transfer band at the transition point would suggest that the low-temperature phase has a crystal structure of a dimeric arrangement of the chloranil anion, as in the case of monomeric-dimeric transition of the Würster's blue perchlorate. In this connection, it is interesting to see that, in the b-axis spectrum observed at a low temperature, a shoulder appeared at about 25×10^3 cm^{-1}. The chloranil anion dimer formed in solution has been reported to give a charge-transfer band at 14.9×10^3 cm^{-1} and a local excitation band at 26.3×10^3 cm^{-1}.[5] It is possible that the 25×10^3 cm^{-1} shoulder is the one corresponding to the 26.3×10^3 cm^{-1} band of the dimer. It would be of particular interest to examine if this shoulder grows up at a lower temperature. Unfortunately, however, we were not able to confirm this because of the limitation of our experimental set-up.

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16) The magnetic susceptibility data used here are those measured by Mr. T. Mizoguchi in our laboratory by means of a Faraday-type magnetic balance.

17) T. Sakata and S. Nagakura, This Bulletin, **42**, 1497 (1969).