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Temperature Dependence of the Dielectric Constants of Potassium-Chloranil Salt and Würster's Blue Perchlorate

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The dielectric constants of potassium-chloranil salt(K^+CA^-) and Würster's blue perchlorate (WBP) were measured around their phase-transition temperatures in the X-band microwave region. In the case of K^+CA^-, a sudden increase in the dielectric constant was observed accompanying a change to the low-temperature phase. This is interpreted to arise from the change in electronic polarization associated with a marked increase in the intensity of the charge-transfer band in the near-infrared region. An anomalous peak and associated gradual changes were observed in the temperature dependence of the dielectric constant of WBP around the phase transition temperature. The difference in dielectric behavior of these two cases is discussed in relation to the optical absorption spectra and other properties of the crystals.

Although the electronic polarizability of a molecular crystal is affected, more or less, by the electronic interaction between molecules, the effect on the dielectric behavior of molecular crystals has usually been regarded as being of minor importance. However, recent investigations on the dielectric properties of crystals of solid charge-transfer complexes and radical salts have revealed several examples where the charge-transfer interaction between molecules plays an important role in determining their dielectric properties.[1,2]

We previously reported the results of dielectric constant measurement on a series of solid molecular complexes containing tetracyanoquinodimethane (TCNQ) as an electron acceptor, pointing out that, when there is a strong low-energy charge-transfer band in the crystal spectrum of a molecular complex, the dielectric constant of the crystal is larger than the value expected by assuming the additivity of molecular polarizations of the constituent molecules.[1]

In the case of the potassium-chloranil salt (K^+CA^-), the crystal spectrum exhibits a near-infrared absorption band associated with the charge-transfer interaction between chloranil ions, the intensity of this charge-transfer band markedly increasing when the crystal is cooled down below the transition point where the crystal changes from the high-spin state to the low-spin state.[3] A similar temperature dependence of the intensity of low-energy charge-transfer band can be observed in the case of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine(TMPD) perchlorate (Würster's blue perchlorate, WBP).[4] Thus it is of particular interest to examine the dielectric behavior of these solids in the vicinity of transition point to see if their dielectric constants increase with the increase of the intensity of low-energy charge-transfer band.

Experimental

The dielectric constants of K^+CA^- and WBP, in the X-band microwave region, were measured by the cavity perturbation method by using a variable-temperature cylindrical cavity of TM_{012} resonance mode with an operation frequency of 9.4 GHz. The structure of the apparatus is shown in Fig. 1. The sample, in the form of a fine crystalline powder, was packed in a thin fused-quartz tube (A in Fig. 1) which was inserted at the middle of the resonance cavity (H). The cavity was cooled by introducing cold nitrogen gas into the copper tube (B) wound around the copper block (E) installed at the top of the cavity. The temperature of the cavity was controlled by adjusting the flow rate of the cold nitrogen gas and/or by using an electric heater (F). We measured the resonance frequencies of the cavity without and with the sample, f_1 and f_2 respectively, at each temperature, and obtained the value $(f_1^2-f_2^2)/f_2^2$. The latter quantity can be assumed to be proportional to $(\varepsilon-1)$ in the first order approximation, where ε is the dielectric constant of the sample.[5,6] It was difficult to estimate the absolute value of dielectric constant from the above experiment because of the difficulty in avoiding the inhomogeneity as regards the packing of sample powder in the tube. Thus, we separately estimated the actual dielectric constant of the sample at room temperature by the method described previously,[5] using a rectangular cavity of TE_{105} mode.

The crystalline powder of WBP was prepared by the method of Michaelis and Granik.[7] The crystalline powder

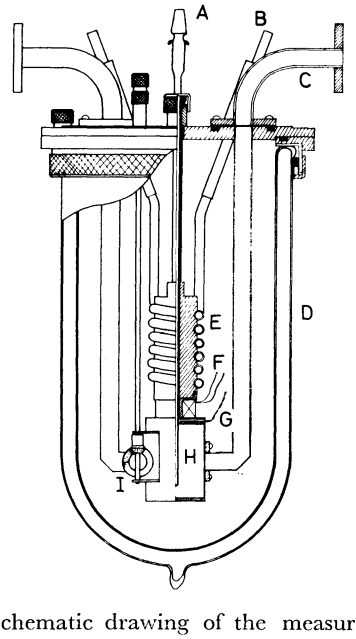

Fig. 1. A schematic drawing of the measuring apparatus.
A; sample tube, B; cold gas inlet, C; wave guide, D; Dewar's vessel, E; copper block, F; heater, G; thermocouple, H; TM_{012} cavity, I; coupling adjuster.

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of K^+CA^- was obtained by the method reported by Torrey and Hunter.[8] The results of elementary analysis agreed with the calculated values in both cases. Since K^+CA^- is known to form hydrate by absorbing moisture from the atmosphere,[9] the sample was carefully dried in a vacuum so that it was completely converted into anhydrous modification. The X-ray diffraction pattern of the powder sample thus obtained was confirmed to agree with that of the anhydrous state. In order to avoid a change of the sample into hydrous modification, the sample tube of dielectric constant measurement was pumped to the vacuum of 10^{-3} Torr soon after the sample powder had been packed into it.

Differential scanning calorimetry (DSC) was carried out on each sample with a Rigaku low-temperature DSC apparatus.

The polarized absorption spectra of single crystals were measured with a microspectrophotometer with a small cryostat at the specimen stage of the microscope system.

Results and Discussion

Figure 2a shows the plot of the frequency shift, $(f_1^2-f_2^2)/f_2^2$, against temperature in the case of K^+CA^-. An approximate scale of dielectric constant is given[10] on the right-hand side. This was determined by normalizing $(f_1^2-f_2^2)/f_2^2$ to the room temperature value of dielectric constant determined by the separate experiment.

On lowering the temperature, the frequency shift remains almost constant (at the value corresponding to the dielectric constant of about 3.5) from room temperature down to about 220 K, then exhibits a sudden increase in the 220—210 K region, and after showing a maximum at 210 K, it stays constant at lower temperatures.[11] On elevating the temperature, however, the frequency shift stays constant up to 260 K, where it shows a sudden decrease, showing a hysteresis in its temperature dependence.

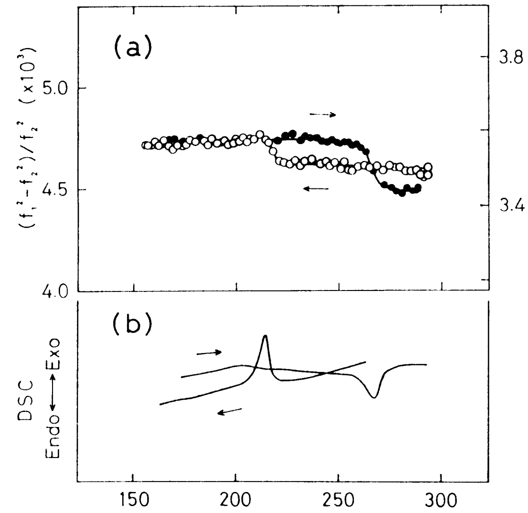

Fig. 2. (a) Temperature dependence of the dielectric constant of potassium-chloranil salt (K^+CA^-). $(f_1^2-f_2^2)/f_2^2$ is plotted as the ordinate, where f_1 and f_2 are the resonance frequencies of the microwave cavity without and with the sample respectively. An approximate scale of the dielectric constant is shown in the right hand side. (b) Differential scanning calorimetry curves of K^+CA^-.

The temperature dependence of the magnetic susceptibility is known to also exhibit an appreciable hysteresis between the heating and cooling processes; the phase transition occurs at 210 K on lowering the temperature, and at 260 K on elevating the temperature.[12,13] This difference of transition temperature is also clearly observable in the DSC curves (Fig. 2b). By comparing Figs. 2a and 2b, we note that the temperature, at which a sudden change of frequency shift occurs, exactly coincides with the transition point, for both the cooling process and heating process.

According to Konno *et al.*,[14] in the high-temperature phase of K^+CA^-, CA^- ions are stacked face-to-face on each other along the c-axis with uniform intermolecular separation, K^+ ions being located at the sites between CA^- columns. Although the details of the crystal structure of the low-temperature phase are not known, it has been inferred that the arrangement of CA^- ions in the CA^- column changes to a dimeric one in the low-temperature phase.[3,9]

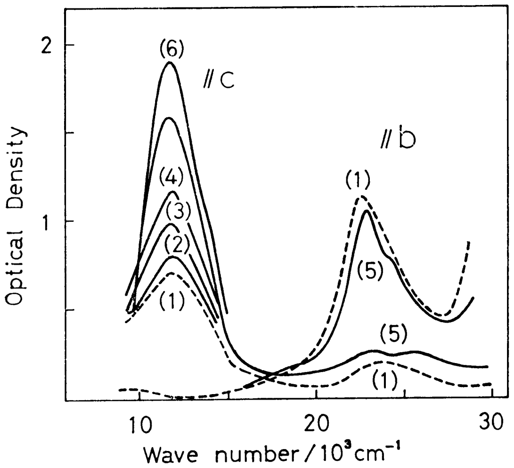

Fig. 3. Temperature dependence of the crystal spectra of the potassium-chloranil salt. (1); 297 K, (2); 280 K, (3); 240 K, (4); 218 K, (5); 209 K, (6); 163 K. (//b and //c denote the b- and c- axis spectrum, respectively).

The crystal spectrum of K^+CA^- is reproduced in Fig. 3.[3] The near-infrared absorption band, at 11.5×10^3 cm^{-1}, is almost completely polarized in the c-axis direction, and has been assigned to the band associated with the charge-transfer interaction between neighboring CA^- ions. As shown in Fig. 3, the intensity of this charge-transfer band markedly increases on lowering the temperature in the vicinity of transition point. Other absorption bands which are associated with the electronic transitions of the CA^- ion are not significantly affected by temperature.

The static electronic polarizability α_e of a semiconductive (or insulating) solid can be related to the electronic transitions of the solid as follows:

$$\alpha_e = \frac{e^2}{4\pi^2 m}\sum_j \frac{f_j}{\nu_j^2}, \tag{1}$$

where ν_j and f_j are the frequency and oscillator strength, respectively, of the j-th electronic transition of the solid.[15)] We see that if there is any low-frequency electronic transition with a strong oscillator strength, it will make a considerable contribution to the electronic polarizability.

In order to consider the relation between the low-frequency charge-transfer band and the electronic polarizability of K^+CA^-, we rewrite Eq. 1 as follows:

$$\alpha_e = \frac{e^2}{4\pi^2 m}\frac{f_{CT}}{\nu_{CT}^2} + \frac{e^2}{4\pi^2 m}\sum_j \frac{f_j}{\nu_j^2} \qquad (2)$$

where the first term represents the contribution of the charge-transfer transition, and the second term those of other electronic transitions. The crystal spectrum of K^+CA^- exhibits a significant change in the vicinity of transition point only in the region of the charge-transfer band. Thus, one can reasonably assume that the second term of Eq. 2 must be almost the same at temperatures above and below transition point, so that the temperature dependence of the electronic polarizability in the vicinity of transition point will be determined mainly by the change in the first term. In other words, the electronic polarizability is expected to vary parallel to the intensity change of the charge-transfer band. Consequently, we can anticipate that the dielectric constant of K^+CA^- suddenly increases as the crystal changes from the high-temperature phase to the low-temperature phase if its change in the vicinity of transition point is primarily dependent on the variation of the electronic polarizability. This prediction is in agreement with observation. Naturally the dielectric constant of a solid depends not only on electronic polarization but also on atomic and lattice polarizations. At present, we can not exclude the possibility that the observed change of dielectric property of K^+CA^- in the vicinity of transition point is to some extent due to the change in the latter polarizations. But, as we will discuss later in comparison with the dielectric behavior of WBP, the electronic polarization is likely to play a dominant role in determining the observed dielectric behavior of K^+CA^- at transition point.

In the case of WBP, we obtained the results shown in Fig. 4a. The frequency shift, $(f_1^2-f_2^2)/f_2^2$, is almost constant down to 250 K, then gradually increases on lowering the temperature, and reaches a maximum value at 190 K. On undergoing the phase transition, it exhibits a sudden decrease, and thereafter, it gradually decreases on lowering the temperature.[16)] In contrast to the corresponding plot of K^+CA^-, there appears no hysteresis in this case between the cooling and heating processes; the plot for both processes exhibits exactly the same temperature dependence. The situation is the same in the DSC experiment as shown in Fig. 4b.

Extensive investigasions have been carried out on the nature of the phase transition of WBP at 190 K, where WBP changes from the high-spin state at higher temperature to the low-spin state at lower temperature.[4,17–21)] It was inferred from these studies that in the low-temperature phase the $TMPD^+$ column along the a-axis consists of a dimeric array of $TMPD^+$ ions, while it has a monomeric array of the ions in the high-temperature phase. The structural change was recently confirmed by crystal structure analysis.[22,23)]

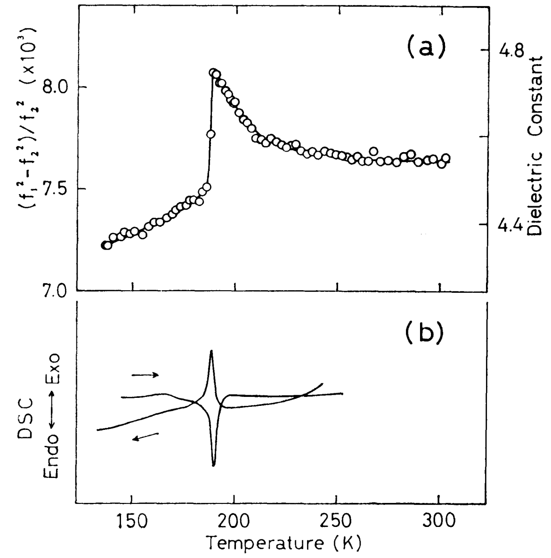

Fig. 4. (a) Temperature dependence of the dielectric constant of Würster's blue perchlorate (WBP). The change in the resonance frequency of the microwave cavity is plotted as the ordinate in the same manner with Fig. 2. An approximate scale of the dielectric constant is also shown in the right hand side. (b) Differential scanning calorimetry curves of WBP.

The polarized absorption spectrum of the WBP crystal is shown in Fig. 5. All the absorption bands in the b- and a-axes spectra at 297 K are attributable to the local-excitations associated with the electronic transitions of $TMPD^+$ ion. No strong absorption band can be found below 15×10^3 cm^{-1} at this temperature. However, as the temperature is lowered below the transition point, a new absorption band grows up at 12.5×10^3 cm^{-1} in the a-axis spectrum. The intensity of this band increases gradually over a wide temperature range on lowering the temperature. The corresponding absorption band has been observed at low temperatures also in the absorption spectrum of a polycrystalline sample of WBP, and attributed to the charge-transfer between $TMPD^+$

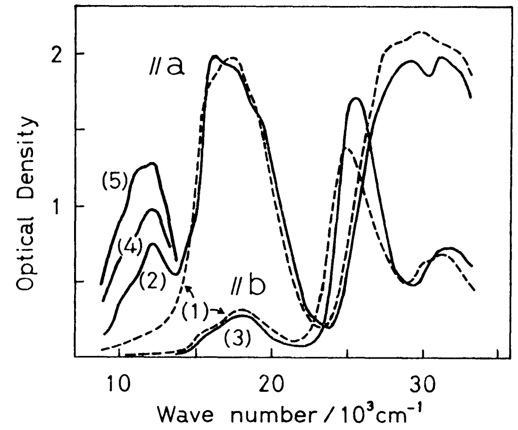

Fig. 5. Temperature dependence of the crystal spectra of Würster's blue perchlorate. (1); 285 K, (2); 138 K, (3); 134 K, (4); 122 K, (5); 83 K. (//a and //b denote the a- and b-axis spectrum, respectively.)

ions.[4] The fact that the above band is completely polarized in the direction of the TMPD$^+$ column, as revealed by the present study, indicates that it is indeed a charge-transfer band associated with the interaction between TMPD$^+$ ions in the TMPD$^+$ column.

Apparently, the change of the absorption spectrum of the WBP crystal accompanying the phase transition is very similar to that of the K$^+$CA$^-$ crystal. Our discussion on the electronic polarizability of the K$^+$CA$^-$ crystal should therefore be also applicable to the case of WBP. Since, as in K$^+$CA$^-$, the intensity of the low-frequency charge-transfer band of WBP markedly increases below the transition point while those of other absorption bands hardly change at all between above and below the transition point, it should be considered that the electronic polarizability of WBP increases in the low-temperature phase. The dielectric constant should thus be expected to increase as the temperature is lowered below the transition point, if the temperature dependence of dielectric constant is determined by the change in the electronic polarizability. However, the temperature dependence of frequency shift observed for WBP in the vicinity of transition point is just the contrary to that mentioned above (Fig. 4a), and quite different from that observed for K$^+$CA$^-$. This seems to indicate that the change of the dielectric constant of WBP is mainly determined by some other factor. The dielectric property of a solid is dependent not only on electronic polarization but also on atomic and lattice polarizations. However, it is very unlikely for atomic polarization to play the determining role for the relatively large change of dielectric constant as observed in the case of WBP at the transition point. In Fig. 4a, we note two features; a sudden decrease at the transition point, and gradual changes above and below this temperature. A similar type of temperature dependence of dielectric constant is known to occur in a crystal containing a component with an electric dipole when the rotational motion of the polar group (or molecule) is allowed above the transition point, but not in the low-temperature phase.[24] However, such a model associated with the orientational polarization can not be applied in the case of WBP.

Generally, in an ionic crystal, the lattice polarization arising from the displacement of ions makes a significant contribution to the static dielectric constant. The magnitude of this contribution is dependent on the frequency of lattice vibration. Recently, Terauchi[25] observed a diffuse X-ray reflection on the WBP crystal at temperatures above the transition point. As the temperature is lowered, the intensity of this reflection increases in proportion to $1/(T-T_c)$, where T_c is a critical temperature close to the transition point. The above reflection is interpreted to arise from the fluctuating dimerization of TMPD$^+$ ions in the TMPD$^+$ column. The fluctuation of β, the angle between the a- and c-axes, is also found to occur in the same temperature range. It is therefore inferred that some optical modes of lattice vibration are softened in the same temperature range. If this is the case, one could expect an anomaly concerning the lattice polarization. Seemingly, the increase of dielectric constant observed in the high-temperature phase of WBP on approaching the transition point is attributable to the above mechanism. On passing through the transition point, the lattice vibrational modes are considered to change suddenly, but the fluctuation of lattice may remain even in the low-temperature phase in the temperature region close to the transition point. The sudden decrease of the dielectric constant at the transition point and the gradual decrease below this point could be understood by this mechanism.

The dielectric behavior in the vicinity of transition point shows a marked difference between K$^+$CA$^-$ and WBP although the phase transitions of these solids resemble each other in many respects. Two possible causes for the difference might be considered as follows. First, in the case of WBP the charge-transfer band appears at a frequency close to that of a strong local-excition band, while in the case of K$^+$CA$^-$ it is very much lower than any of the local-excitation bands. The intensity change of the charge-transfer bands of WBP takes place gradually over a relatively wide temperature range, whereas that of K$^+$CA$^-$ varies steeply on phase transition. Thus, the intensity change of charge-transfer band is expected to give a smaller effect on electronic polarizability in the case of WBP as compared with K$^+$CA$^-$. Second, we may consider that the contribution of lattice polarization is considerably larger in WBP than in K$^+$CA$^-$. In WBP, the heavy and bulky ClO_4^- ion is loosely bound to the TMPD$^+$ column, so that there can be a low-frequency lattice-vibrational mode giving a significant contribution to the lattice polarization. In K$^+$CA$^-$, the K$^+$ ion is rather tightly bound to the CA$^-$ column through the interaction with the oxygen atoms of the neighboring CA$^-$ ions. In effect, the dielectric constant of WBP, about 4.5 at room temperature, is much larger than that usually obtained for organic crystals composed of neutral molecules, and is comparable to those of inorganic ionic crystals. On the other hand, the dielectric constant of K$^+$CA$^-$ at room temperature is 3.5, which is comparable to that obtained in the cases of non-ionic charge-transfer complexes involving polycyclic aromatic hydrocarbons as the donor and TCNQ as the acceptor. This indicates that lattice polarization makes a significant contribution to the dielectric constant in the case of WBP, but not in the case of K$^+$CA$^-$.

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powder sample. Since $(\varepsilon_a - 1)$ is proportional to $\delta \cdot (\varepsilon - 1)$ when the volume fraction of crystals in the powder sample is expressed by δ, the frequency shift must be proportional to $(\varepsilon - 1)/\rho$, where ρ is the crystal density. This means that, if there is an appreciable change in ρ, the observed variation of frequency shift does not directly show the actual change of dielectric constant which must be dependent of the change of crystal density, but shows the variation of polarization after correction has been done as regards the change of crystal density.

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