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The Semiconductive Property and the Phase Transition of the $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^{\cdot}$ Anion Radical Salt. The Entropy Change Due to Electrons and Holes

Yôichi IIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The semiconductive organic crystal of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ is known to undergo a first-order phase transition at 315.7°K. The discontinuity in the temperature dependence of the electrical conductivity takes place at the transition temperature, above which the populations of the electrons and the holes in the electrical conductivity increase abruptly. A theoretical consideration of the system of conduction carriers in an intrinsic semiconductor was developed in order to evaluate the entropy change of the electrons and holes at the phase transition. For $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^-$, this kind of entropy change was found to be much less than the total entropy change determined from the heat-capacity measurements by Kosaki *et al.* In view of these results, it was concluded that the anomaly in the electrical conductivity was induced by the change in the crystal structure.

There are a few organic semiconductors that are known to undergo phase transitions.[1,2] The phase transitions of such organic semiconductors are particularly interesting, since the anomalies in their electrical conductivities are associated with their phase transitions.

Much attention has been paid to the solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) because of their high electrical conductivities.[1-4] The phase transition of the TCNQ anion radical salt of methyltriphenylphosphonium, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, is known to take place at 315.7°K.[1,5-7] Heat-capacity measurements of this phase transition have been made by Kosaki *et al.*[7] The transition has thus been found to be of the first order. The enthalpy and the total entropy change associated with the phase transition were experimen-

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[1] Y. Iida, M. Kinoshita, M. Sano, and H. Akamatu, This Bulletin, **37**, 428 (1964).

[2] Y. Iida, *J. Phys. Soc. Jap.*, **30**, 583 (1971).

[3] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson, and W. E. Mochel, *J. Amer. Chem. Soc.*, **84**, 3373 (1962).

[4] W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39**, 3523 (1963).

[5] R. G. Kepler, *ibid.*, **39**, 3528 (1963).

[6] Y. Iida, M. Kinoshita, A. Kawamori, and K. Suzuki, This Bulletin, **37**, 764 (1964).

[7] A. Kosaki, Y. Iida, M. Sorai, H. Suga, and S. Seki, *ibid.*, **43**, 2280 (1970).

tally determined to be 485.18 cal/mol and 1.7206 cal/deg·mol respectively.

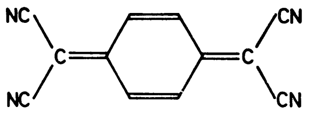

Fig. 1. 7,7,8,8-Tetracyanoquinodimethane (TCNQ).

On the other hand, the discontinuity in the temperature dependence of the electrical conductivity of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ was observed at the transition temperature, where the electrical conductivity increased abruptly by a factor of about 3.5 in the higher temperature range.[1] This change was found to be reversible. If this anion radical salt belongs to an intrinsic semiconductor, the temperature dependence of the electrical conductivity, σ, below or above the transition temperature can be expressed by:

$$\sigma = \sigma_0 \exp(-E_g/2\boldsymbol{k}T), \tag{1}$$

where E_g is the energy gap between the conduction band and the valence band. The energy gap in the low-temperature phase, E_g, was experimentally determined to be 0.82±0.04 eV, while that in the high-temperature phase, E_g', was thus determined to be 0.60±0.04 eV.[1] An appreciable decrease in the energy gap by about 0.22 eV in the high-temperature phase was found to be caused by the phase transition. Therefore, at the transition temperature, the abrupt increase in the electrical conductivity in the higher temperature range can be understood mostly in terms of the increase in the population of conduction carriers in the high-temperature phase. At this time, the abrupt increase in the electrons and the holes should cause some entropy creation at the phase transition.

The purpose of the present paper is to examine to what extent this kind of entropy change contributes to the total entropy change as determined by the heat-capacity measurements. For this purpose, a general statistical theory for the system of electrons and holes in an intrinsic semiconductor will be developed in the Theoretical section. The entropy change due to the electrons and holes was evaluated when a first-order phase transition takes place in the semiconductor. By applying this theory to the phase transition of $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^-$, we shall investigate the mechanism of the phase transition of this anion radical salt.

Theoretical

Let us consider, in general, the system of an intrinsic semiconductor, where the energy gap between the conduction band and the valence band is assumed to be E_g. In the case of a usual organic semiconductor, the band widths of both the conduction band and the valence band are narrow enough in comparison with the energy gap.[8,9] The carriers for the electrical conduction are excited electrons in the conduction band and holes in the valence band. For an intrinsic semiconductor, the number of the electrons is equal to that of the holes.

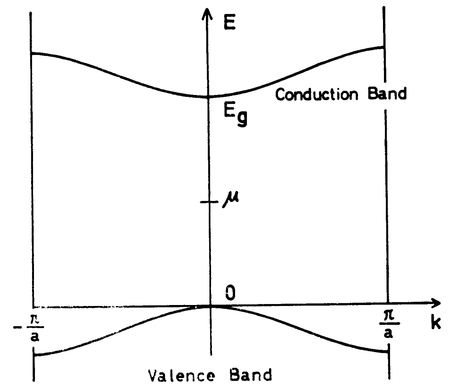

Fig. 2. A schematic representation of the band structure of an intrinsic semiconductor. The zero energy level is taken at the top of the valence band. E_g is the energy gap between the conduction band and the valence band, and μ is the level of the Fermi energy.

Electrons in Conduction Band. First, let us proceed to consider the electrons in the conduction band. It is convenient to describe this system as a grand canonical ensemble.[10] The grand partition function, Z_G, at the temperature T is represented by:

$$Z_G = \sum_{n_i} \exp(-\beta \sum_i \varepsilon_i n_i), \tag{2}$$

$$\varepsilon_i = E_i - \mu, \qquad \beta = \frac{1}{\boldsymbol{k}T}, \tag{3}$$

where the sum with i runs over all the conceived quantum states. In the i th quantum state, E_i is the energy of an electron and n_i represents the number of electrons. μ is the chemical potential (*i.e.*, the Fermi energy). For the Fermi-Dirac statistics, since $n_i=0$ or 1,

$$Z_G = \prod_i (1 + e^{-\beta\varepsilon_i}). \tag{4}$$

The entropy of the system of the electrons in the conduction band, S(electron), can be derived from:

$$S(\text{electron}) = \frac{\partial}{\partial T}\left(\frac{1}{\beta}\ln Z_G\right)_{V,\mu} = \boldsymbol{k}\sum_i \ln(1+e^{-\beta\varepsilon_i}) + T^{-1}\sum_i (e^{\beta\varepsilon_i}+1)^{-1}\varepsilon_i. \tag{5}$$

By using the form of the Fermi-Dirac distribution function of $f_i = 1/(e^{\beta\varepsilon_i}+1)$, S(electron) is expressed as:

$$S(\text{electron}) = -\boldsymbol{k}\sum_i [f_i \ln f_i + (1-f_i)\ln(1-f_i)]. \tag{6}$$

The first Brillouin zone in the conduction band is composed of N conduction levels, each of which includes α and β spin states. Then,

$$S(\text{electron}) = -2\boldsymbol{k}\sum_{i=1}^{N} [f_i \ln f_i + (1-f_i)\ln(1-f_i)]. \tag{7}$$

In Eq. (3), the energy of the electron in the conduction band, E_i, and the Fermi energy of the intrinsic semiconductor, μ, are;

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[8] O. H. LeBlanc, *J. Chem. Phys.*, **33**, 626 (1960); R. G. Kepler, Org. Semicond. Proc. Inter-Ind. Conf., 1 (1962).

[9] O. H. LeBlanc, *J. Chem. Phys.*, **35**, 1275 (1961); R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, Jr., *ibid.*, **42**, 733 (1965).

[10] C. Kittel, "Elementary Statistical Physics," John Wiley & Sons, New York (1958).

$$E_i = E_g + \frac{\boldsymbol{\hbar}^2\boldsymbol{k}_i^{\,2}}{2m_e}, \tag{8}$$

$$\mu = \frac{1}{2}E_g + \frac{3}{4}\boldsymbol{k}T\ln\frac{m_h}{m_e}, \tag{9}$$

where $\boldsymbol{\hbar}^2\boldsymbol{k}_i^{\,2}/2m_e$ is the kinetic energy of the electron and is related to the conduction band structure, and where m_e or m_h is the effective mass of the electron or the hole respectively. In the case of usual organic semiconductors, although it is very difficult to determine the precise band structures, the band widths of both the conduction band and the valence band are of the order of $\boldsymbol{k}T$.[8,9] Since E_g is much larger than $\boldsymbol{k}T$, one can neglect, in Eq. (8), $\boldsymbol{\hbar}^2\boldsymbol{k}_i^{\,2}/2m_e$ in comparison with E_g, and μ is very nearly equal to $\frac{1}{2}E_g$. By the use of these approximations, the Fermi-Dirac distribution function of f_i is replaced by:

$$f = f_i \approx \frac{1}{\exp(E_g/2\boldsymbol{k}T)+1}, \quad (i=1,2,\cdots,N). \tag{10}$$

Therefore, from Eq. (7), we have:

$$S(\text{electron}) = -2N\boldsymbol{k}[f\ln f + (1-f)\ln(1-f)]. \tag{11}$$

Holes in Valence Band. The holes in the valence band can be treated in a way similar to that of the electrons in the conduction band. In the case of the holes in the valence band, the Fermi-Dirac distribution function is:

$$f_i = \frac{1}{e^{-(E_i-\mu)/\boldsymbol{k}T}+1}. \tag{12}$$

Here, the energy of a hole, E_i, in the valence band is:

$$E_i = -\frac{\boldsymbol{\hbar}^2\boldsymbol{k}_i^{\,2}}{2m_h}. \tag{13}$$

If we assume that E_g is much larger than $\boldsymbol{\hbar}^2\boldsymbol{k}_i^{\,2}/2m_h$,

$$f = f_i \approx \frac{1}{\exp(E_g/2\boldsymbol{k}T)+1}, \quad (i=1,2,\cdots,N). \tag{14}$$

In this case, the entropy of the system of the holes in the valence band, S(hole), is found to be identical with that of the electrons in Eq. (11).

Entropy Change Associated with a First-order Phase Transition. By summing S(electron) and S(hole), the entropy per mol for the system of the conduction carriers in an intrinsic semiconductor, S(carrier), is then expressed as:

$$\begin{aligned} S(\text{carrier}) &= S(\text{electron}) + S(\text{hole}) \\ &= -4\boldsymbol{R}[f\ln f + (1-f)\ln(1-f)]. \end{aligned} \tag{15}$$

Let us now consider the case when a first-order phase transition takes place in the intrinsic semiconductor at the temperature, T_c. The energy gaps for the low-temperature phase and the high-temperature phase are assumed to be E_g and E_g' respectively. At the transition temperature, the Fermi-Dirac distribution function, f, and the entropy for the system of the conduction carriers, S(carrier), in the low-temperature phase can be derived from the T_c and E_g values by means of Eqs. (10) and (15), while those in the high-temperature phase, f' and S'(carrier), can be derived from the T_c and E_g' values. Therefore, for the system of the conduction carriers, the entropy change, ΔS(carrier), at the phase transition is estimated to be:

$$\Delta S(\text{carrier}) = S'(\text{carrier}) - S(\text{carrier}). \tag{16}$$

Application of the Theory to the Phase Transition of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$

In this section, the above-mentioned theory will be applied to the phase transition of the anion radical salt of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ at T_c=315.7°K. For this anion radical salt, as has been described in the Introduction, the energy gap between the conduction band and the valence band in the low-temperature phase, E_g, is 0.82±0.04 eV, while that in the high-temperature phase, E_g', is 0.60±0.04 eV.[1] Therefore, these values well fulfill the condition that both E_g and E_g' should be considerably larger than $\boldsymbol{k}T_c$. The notations described in the preceding section will be used for f, S(carrier), f', and S'(carrier). From Eq. (10), f and f' at the transition temperature are evaluated approximately by:

$$f \approx \exp(-E_g/2\boldsymbol{k}T_c), \tag{17}$$

$$f' \approx \exp(-E_g'/2\boldsymbol{k}T_c). \tag{18}$$

Putting the values of f and f' into Eq. (15), we have;

$$S(\text{carrier}) = 3.7\times10^{-5}\ \text{cal/deg}\cdot\text{mol}, \tag{19}$$

$$S'(\text{carrier}) = 1.5\times10^{-3}\ \text{cal/deg}\cdot\text{mol}. \tag{20}$$

Therefore, for the phase transition of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, the molar entropy change due to the electrons and holes for the electrical conduction is estimated to be:

$$\Delta S(\text{carrier}) = 1.5\times10^{-3}\ \text{cal/deg}\cdot\text{mol}. \tag{21}$$

Discussion

The above-mentioned results clearly indicate that, in the phase transition of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, the magnitude of $\Delta S(\text{carrier})=1.5\times10^{-3}$ cal/deg·mol is negligibly small in comparison with that of the total entropy change, $\Delta S(\text{obs})=1.7206$ cal/deg·mol, as determined from the heat-capacity measurements.[7] This means that it is quite hopeless to consider the system of the electrons and the holes in the electrical conduction as the main source of entropy creation at the transition. Therefore, most of the total entropy change was found to arise from other sources.

Let us examine the entropy change in the magnetic spins associated with the unpaired electrons on the TCNQ anion radicals. Obviously, the $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ anion radical salt is composed of the diamagnetic counter cations, TCNQ anion radicals, and formally neutral TCNQ molecules.[3-5] The magnetic spins ($S=1/2$) on the TCNQ anion radicals are known to be paired up by an exchange interaction.[5] This system contains a singlet ground state and a triplet exciton state. However, Kepler found a sharp discontinuity in the temperature dependence of the paramagnetic susceptibility of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ at the transition temperature.[5] Chesnut showed that a certain type of order-disorder transition with respect to the triplet exciton density does occur if one includes in the interaction a term which is quadratic in the triplet exciton density, ρ.[11] In this case, the spin entropy change, ΔS(spin), associated with the phase transition is:

$$\Delta S(\text{spin}) = \tfrac{1}{2}\boldsymbol{R}\Delta\rho \ln 3, \tag{22}$$

where $\Delta\rho$ is the change in the triplet exciton density at the transition. In a previous paper,[12] the present author estimated the value of ΔS(spin) for the phase transition of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^{\bar{\cdot}}$ to be 0.13 cal/deg·mol by the use of $\Delta\rho=0.12$, which was calculated from Kepler's data on the discontinuity in the paramagnetic susceptibility at the transition temperature.[5] Although the value of ΔS(spin) is appreciably larger than that of ΔS(carrier), the value of ΔS(spin) is again much less than that of ΔS(obs).

The above-mentioned investigations indicate that the rest of the entropy change, ΔS(obs)$-\Delta S$(carrier)$-\Delta S$(spin)$=1.59$ cal/deg·mol, should be ascribed to the entropy change due to the change in the crystal structure. It is important to note that the magnitude of this residual entropy change amounts to 92.4% of the total entropy change of ΔS(obs). In view of these results, we may conclude that the phase transition of the anion radical salt of $[(C_6H_5)_3PCH_3]^+$-$(TCNQ)_2^{\bar{\cdot}}$ at 315.7°K comes mostly from some structural changes. The anomalies in the electrical conductivity and in the paramagnetic susceptibility are probably induced by the change in the crystal structures.

Concluding Remarks

For such semiconductors as $[(C_6H_5)_3PCH_3]^+$-$(TCNQ)_2^{\bar{\cdot}}$, where the energy gap is considerably larger than $\boldsymbol{k}T$, the magnitude of the entropy for the system of the electrons and holes in the electrical conduction is negligibly small, since the distributions of the electrons in the conduction band and of the holes in the valence band are quite limited at the temperature T.

On the other hand, however, the carrier population is very much increased for semiconductors in which the energy gap is comparable to $\boldsymbol{k}T$. In this case, the magnitude of the entropy for the system of the electrons and holes becomes appreciably large. If these semiconductors undergo phase transitions, this kind of entropy should make a significant contribution to the mechanism of the phase transitions. In addition to the increase in the carrier population, the level of the Fermi energy in Eq. (9) is not located at the center between the conduction band and the valence band. Therefore, Eq. (14) for the holes in the valence band is no longer identical with Eq. (10) for the electrons in the conduction band. Since one cannot neglect the term of $\hbar^2\boldsymbol{k}_i^2/2m_e$ in Eq. (8) or that of $\hbar^2\boldsymbol{k}_i^2/2m_h$ in Eq. (13) in comparison with that of E_g, exact knowledge concerning the band structures of both the conduction band and the valence band will be required in order to evaluate the entropy due to the electrons and the holes.

The author would like to express his appreciation to Professor Akiko Ohno for her helpful discussions.

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11) D. B. Chesnut, *J. Chem. Phys.*, **40**, 405 (1964).

12) Y. Iida, This Bulletin, **43**, 3685 (1970).