BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 2880—2881 (1973)

Phase Transition in Organic Semiconductor. Entropy Change Due to Conduction Carriers

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(Received June 16, 1973)

There are a few organic semiconductors that are known to undergo phase transitions. The phase transitions of such materials are particularly interesting, because the anomalies in their electrical conductivities are associated with the phase transitions.[1-4] In a previous paper,[3] we studied the entropy for the system of conduction carriers (*i.e.*, electrons and holes) in an intrinsic semiconductor. By the use of a statistical theory, we examined to what extent this kind of entropy contributes to the total entropy change of the phase transition as determined from the heat-capacity measurements.

According to this theory, for an intrinsic semiconductor with very narrow band width, the magnitude of the entropy for the system of conduction carriers at temperature, T, is expressed by

$$S(\text{carrier}) = -4R\{f \ln f + (1-f) \ln (1-f)\}, \quad (1)$$

where $f \approx 1/\{\exp(E_g/2kT)+1\}$; E_g is the energy gap between the conduction band and the valence band. Consider the case when a first-order phase transition takes place in the intrinsic semiconductor at the T_c temperature in the solid state. The energy gaps for the low- and high-temperature phases are assumed to be E_g and E_g', respectively. At the transition temperature, the Fermi-Dirac distribution function, f, and the entropy due to the conduction carriers, S(carrier), in the low-temperature phase can be derived from the T_c and E_g values, while those in the high-temperature phase, f' and S'(carrier), from the T_c and E_g' values. Therefore, for the system of the conduction carriers, the entropy change, ΔS(carrier), associated with the phase transition is estimated to be

$$\Delta S(\text{carrier}) = S'(\text{carrier}) - S(\text{carrier}). \quad (2)$$

Let us consider two possible cases of the phase transitions. The first is of the phase transitions for intrinsic semiconductors where the E_g value in the low-temperature phase exceeds the E_g' value in the high-temperature phase. In this case, since the magnitude of S'(carrier) is larger than that of S(carrier) at $T=T_c$, a certain kind of order→disorder process with respect to the conduction carriers is involved in the phase transition, and the ΔS(carrier) value is positive in going from the low-temperature phase to the high-temperature phase. Therefore, if the phase transition of the semiconductor is endothermic, the ΔS(carrier) term plays a positive or additive contribution to the total entropy change of the phase transition, ΔS(total), as determined from heat-capacity measurements. The first-order phase transition of the semiconductive anion radical salt of $[(C_6H_5)_3PCH_3]^+ (TCNQ)_2^-$, where TCNQ is 7,7,8,8-tetracyanoquinodimethane, at $T_c=315.7$ K corresponds to one of these examples. According to the heat-capacity measurements by Kosaki *et al.*,[5] the enthalpy and the total entropy creation associated with this phase transition were experimentally determined to be 485.18 cal/mol and 1.7206 cal/K·mol, respectively. We have observed, at 315.7 K, a discontinuity in the temperature dependence of the electrical conductivity and a slight crystal volume decrease in the high-temperature phase.[1,4,6] By means of the temperature dependence of the conductivity, the E_g and E_g' values were experimentally determined to be 0.82 ± 0.04 eV and 0.60 ± 0.04 eV, respectively.[1,4] The crystal volume decrease perhaps gives rise to the fact that E_g exceeds E_g'. By the use of Eqs. (1) and (2), we have $\Delta S(\text{carrier})=1.5\times10^{-3}$ cal/K·mol for this phase transition. Therefore, we can evidently see that this positive ΔS(carrier) value contributes to the whole entropy creation of $\Delta S(\text{total})=1.7206$ cal/K·mol by 8.7×10^{-2}%.

The second case is of the phase transitions for intrinsic semiconductor where the E_g value is less than the E_g' value. This kind of phenomenon will be usually observed when a crystal volume increase is caused by the phase transition in the high-temperature phase. At this time, in going from the low-temperature phase to the high-temperature phase, a certain kind of disorder→order change with respect to the conduction carriers takes place at the phase transition, because the magnitude of S(carrier) is definitely larger than that of S'(carrier) at $T=T_c$. Therefore, for the endothermic phase transition of the semiconductor, although its over-all entropy is increased, the entropy for the system of the conduction carriers is decreased, and the ΔS(carrier) term plays a negative contribution to the total entropy change, ΔS(total), of the phase transition. We have to indicate the importance of this phenomenon. For example, the phase transition of crystalline hexamethylbenzene at $T_c=384.1$ K corresponds to this case. For this phase transtioin, the enthalpy change was experimentally determined to be 4.2×10^2 cal/mol, and the total entropy creation is estimated to be 1.1 cal/K·mol.[7,8] On the other hand, Kurematsu

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6) Y. Iida, *ibid.*, to be published.

7) M. E. Spaght, S. B. Thomas, and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).

8) Landort-Börnstein, "Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik, Technik," II Band, 4 Teil, 6 Auflage, Springer-Verlag, Berlin. Göttingen. Heidelberg (1961); Nippon Kagaku-kai, "Kagaku Benran," Maruzen ,Tokyo (1966).

et al. measured the electrical conductivity and the crystal volume of this compound and found, at the transition temperature, an anomaly in the temperature dependence of the conductivity and an abrupt crystal volume increase in the high-temperature phase.[2] They assumed that the hexamethylbenzene crystal belonged to an intrinsic semiconductor, and determined experimentally the energy gaps in the low- and high-temperature phases, E_g and E_g', to be 2.5 and 4.5 eV, respectively. For this compound, the crystal volume increase perhaps gives rise to the fact that E_g is less than E_g'. By putting the E_g, E_g', and T_c values into Eqs. (1) and (2), we have $\Delta S(\text{carrier}) = -1.18 \times 10^{-14}$ cal/K·mol. Therefore, this negative ΔS(carrier) value, although its magnitude is very small, is found to make a negative contribution to the total entropy creation for this phase transition.

For such organic semiconductors as a hexamethylbenzene crystal, where the energy gap is considerably larger than kT, the magnitude of the entropy for the system of the conduction carriers is negligibly small, because the distributions of the electrons in the conduction band and of the holes in the valence band are quite limited at the temperature T. However, for semiconductors in which the energy gap is comparable to kT, the carrier population and, thus, the magnitude of the entropy due to the conduction carriers are very much increased. Consider the case when these semiconductors undergo first-order endothermic phase transitions. If the E_g value in the low-temperature phase is less than the E_g' value in the high-temperature phase, an appreciable amount of negative ΔS(carrier) value due to disorder→order process of the conduction carriers should make a significant negative contribution to the mechanism of the phase transitions. An attempt is currently under way to find such materials.