Molecular Crystals and Liquid Crystals

Phase Transition and Volume Change of Anion Radicals Salts of $[(C_6H_5)_3PCH_3]^+{}_{1-x}[(C_6H_5)_3AsCH_3]^+{}_x(TCNQ)^-{}_2$, $(0 \leq x \leq 1)$

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Version of record first published: 28 Mar 2007.

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Phase Transition and Volume Change of Anion Radical Salts of $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x$ $(TCNQ)^-_{\frac{1}{2}}$, $(0 \leq x \leq 1)$
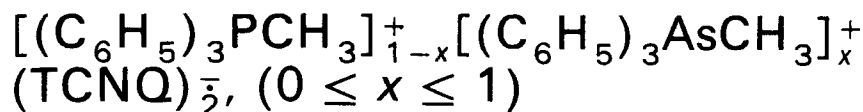
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Our previous thermodynamical approach was reexamined to study phase transition of anion radical salts, $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x(TCNQ)^-_{\frac{1}{2}}$, $(0 \leq x \leq 1)$. The mechanism of the phase transition of the solid solution at 1 atm pressure was confirmed to be $\alpha\gamma \to \beta\gamma$, and the volume change associated with the phase transition was estimated to be $\Delta V = -1.3(1-x)$ cm³/mol.

Much attention has been paid to the solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ), because of their prominent electronic properties.[1–6] In particular, the salts containing mixed cations represented by $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x$ $(TCNQ)^-_{\frac{1}{2}}$, $(0 \leq x \leq 1)$, undergo phase transitions at 1 atm pressure.[1–6] In order to understand the mechanism of the phase transition, we proposed in a previous paper a thermodynamical theory of ideal solid solution model for those TCNQ mixed crystals.[7] According to this theory, there are four possible phases ($\alpha\gamma$, $\beta\gamma$, $\alpha\delta$ and $\beta\delta$) for the solid solutions. Their Gibbs free energies per mol can be expressed by

$$G^{ij}(T, p) = (1 - x)G^i_1(T, p) + xG^j_2(T, p)$$
$$+ RT\{(1 - x)\ln(1 - x) + x \ln x\}, (i = \alpha, \beta; j = \gamma, \delta), \quad (1)$$

where $(1 - x)$ and x are the mole fractions of the component

$$[(C_6H_5)_3 PCH_3]^+(TCNQ)^-_{\frac{1}{2}} \quad \text{and} \quad [(C_6H_5)_3AsCH_3]^+(TCNQ)^-_{\frac{1}{2}},$$
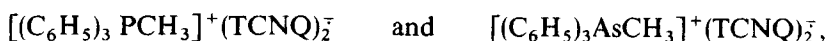
respectively. $G^\alpha_1(T, p)$ and $G^\beta_1(T, p)$ are the Gibbs free energies per mol. for

the low-temperature (α) and high-temperature (β) phases of pure phosphonium salt, while $G_2^\gamma(T, p)$ and $G_2^\delta(T, p)$ are those for ordinary-pressure (γ) and high-pressure (δ) phases of pure arsonium salt, respectively.[1-7]

Hereafter, we only consider the phase transitions of the solid solutions at 1 atm pressure. The low-temperature phase of the solid solutions could be easily assigned to the $\alpha\gamma$ phase, because it forms a uniform phase and faces to the α phase at $x = 0.00$ and to the γ phase at $x = 1.00$.[7] However, there are two possibilities ($\beta\gamma$ or $\beta\delta$) for the high-temperature phase. One of the methods to assign this phase was to examine how ΔH (heat of transition per mol.) and ΔS (entropy change per mol.) associated with the phase transition are related to x (composition parameter) of the solid solution.[7] If the high-temperature phase is $\beta\delta$, $\Delta H = (1 - x)\Delta H_1 + x\Delta H_2$ and $\Delta S = (1 - x)\Delta S_1 + x\Delta S_2$, where $\Delta H_1 = H^\beta - H^\alpha$, $\Delta H_2 = H^\delta - H^\gamma$, $\Delta S_1 = S^\beta - S^\alpha$, $\Delta S_2 = S^\delta - S^\gamma$, and where H^i and S^i, ($i = \alpha, \beta, \gamma$ or δ), are the heat content and the entropy per mol. for each phase, respectively. On the other hand, if the high-temperature phase is $\beta\gamma$, $\Delta H = (1 - x)\Delta H_1$ and $\Delta S = (1 - x)\Delta S_1$. By using differential scanning calorimeter (DSC), we previously obtained the experimental relation of ΔH and ΔS versus x.[3,4] The results clearly supported the latter case, indicating that the high-temperature phase is $\beta\gamma$.[7] However, there was a criticism against this conclusion. Sorai et al. suggested that DSC measurements might catch only a sharp peak of heat-capacity change around the transition temperature and that they found additional broad skirt in their heat-capacity curve.[8] On this basis, they did not support our conclusion. In the present paper, we tried another approach to confirm our previous conclusion.

For this purpose, we examined the crystal volume change (ΔV) due to the phase transition of the solid solution. From Eq. (1), in the case of $\alpha\gamma \to \beta\delta$ transition, $\Delta V = (1 - x)\Delta V_1 + x\Delta V_2$, where $\Delta V_1 = V^\beta - V^\alpha$, $\Delta V_2 = V^\delta - V^\gamma$, and V^i, ($i = \alpha, \beta, \gamma$ or δ), is the crystal volume for each phase. But, for the $\alpha\gamma \to \beta\gamma$ transition, $\Delta V = (1 - x)\Delta V_1$. We previously estimated the ΔV_1 value to be -1.3 cm^3/mol. by using Clausius–Clapeyron equation for the phase transition of pure phosphonium salt,[7] while the ΔV_2 value was estimated to be -3.52 cm^3/mol. by Merkl et al.[2] When the thermal coefficient of volume expansion of the α phase is small and very nearly equal to that of the β phase, and when the coefficient of the γ phase is small and very nearly equal to that of the δ phase, both the ΔV_1 and ΔV_2 values will be practically independent of the temperature. If the high-temperature phase of the solid solution is $\beta\delta$, the ΔV value is the smallest at $x = 0.00$, increases linearly with the increase of x, and has the maximum value at $x = 1.00$. On the other hand, if the high-temperature phase is $\beta\gamma$, the ΔV value is the largest at $x = 0.00$, and decreases linearly with the increase of x, converging to zero at $x = 1.00$. Although measurements of the ΔV value against x will provide

a direct evidence for determining the high-temperature phase, the ΔV value is too small to measure, and we have not yet made such an attempt. However, the experimental results of the anomalies in the electrical and magnetic properties of the solid solutions at the transition temperatures are quite useful for this purpose.

According to our previous conductivity measurements at 1 atm pressure,[6] all the salts except for pure arsonium salt show a sharp discontinuity in the temperature dependence of the electrical conductivity at the transition temperature (T_c), where the conductivity increased abruptly in the high-temperature phase. A lower value of T_c was observed when the temperature was lowered. This is due to the hysterysis of the phase transition. On the basis of these results, the phase transitions of our system are of the first order. We denote $\sigma(T_c)$ and $\sigma'(T_c)$ as the experimental values of the electrical conductivities at T_c in the low- and high-temperature phases, respectively. The quantity of $[\sigma'(T_c) - \sigma(T_c)]/\sigma(T_c)$ is introduced in order to express the magnitude of the discontinuity of the conductivity at T_c. For the solid solutions, the experimental result of this quantity versus x is illustrated in Figure 1,[6] which clearly shows that the discontinuity is the largest at $x = 0.00$, and decreases
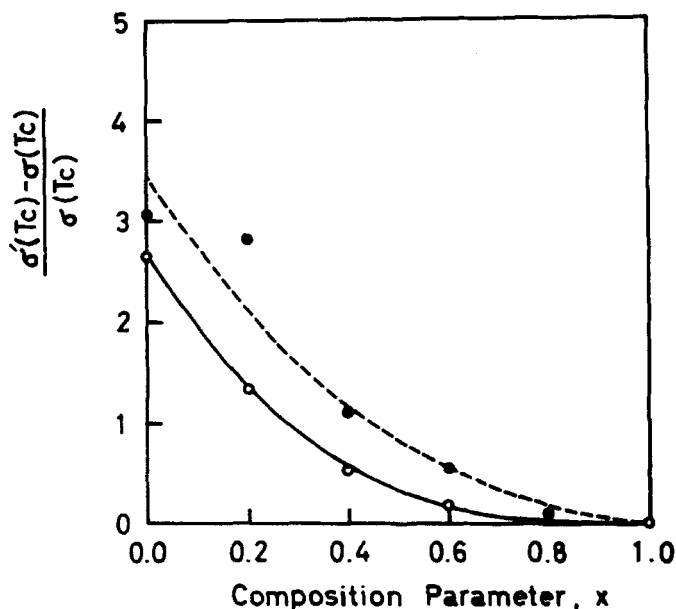

FIGURE 1 The experimental relation of the magnitude of the discontinuity of the electrical conductivity at the T_c temperature, $[\sigma'(T_c) - \sigma(T_c)]/\sigma(T_c)$, to the composition parameter, x, in $[(C_6H_5)_3PCH_3]^+_{1-x}[(C_6H_5)_3AsCH_3]^+_x(TCNQ)^-_2$, $(0 \le x \le 1)$. The unfilled circles indicate the values as the temperature was raised, while the filled circles denote values as the temperature was lowered. See Ref. 6.

progressively with the increase of x, converging to zero at $x = 1.00$. For pure arsonium salt where $x = 1.00$, no discontinuity of the conductivity was observed up to the decomposition temperature. Although it is somewhat difficult to relate quantitatively the $[\sigma'(T_c) - \sigma(T_c)]/\sigma(T_c)$ value to the ΔV value, one can well expect that larger value of ΔV will definitely lead to larger value of $[\sigma'(T_c) - \sigma(T_c)]/\sigma(T_c)$. In this respect, the experimental relation of Figure 1 has the same tendency as $\Delta V = (1 - x)\Delta V_1$ for the $\alpha\gamma \to \beta\gamma$ phase transition. For the $\alpha\gamma \to \beta\delta$ transition, the $[\sigma'(T_c) - \sigma(T_c)]/\sigma(T_c)$ value will increase with the increase of x, and will not converge to zero at $x = 1.00$; thus, this model is not applicable to our experimental results.

The situation is the same for the magnetic properties of those solid solutions. Kepler reported his experimental results on the temperature dependence of the static magnetic susceptibilities, as is shown in Figure 4 of Ref. 1. We obtained quite similar results by the ESR measurements.[5] All the salts except for pure arsonium salt show a sharp discontinuity in the temperature dependence of the magnetic susceptibility. The magnitude of this discontinuity is the greatest at pure phosphonium salt, decreases progressively with the addition of the arsonium cations, and converges to zero at pure arsonium salt. Therefore, the magnetic susceptibility data again support that the high-temperature phase of the solid solution is $\beta\gamma$.

The conclusion of the present work agrees well with that derived previously from the thermodynamic quantities associated with the phase transitions.[7] Finally, we have to mention the volume change due to the $\alpha\gamma \to \beta\gamma$ phase transition of the solid solutions, for which $\Delta V = (1 - x)\Delta V_1$. $\Delta V_1 = V^\beta - V^\alpha = -1.3 \text{ cm}^3/\text{mol.}$ is the value at $T_c = 315.7 \text{ K}$ of pure phosphonium salt. However, according to X-ray analysis by Konno and Saito,[9] both the crystal volume and the structure of the α phase of the phosphonium salt are very similar to those of the β phase. This implies an equality of the thermal coefficients of volume expansion for both phases. Therefore, $\Delta V_1 = -1.3 \text{ cm}^3/\text{mol.}$ still holds at temperatures other than 315.7 K, and the volume change due to the phase transition of the solid solution at 1 atm pressure can be well expressed by $\Delta V = -1.3 (1 - x) \text{ cm}^3/\text{mol.}$ An attempt is currently under way to determine experimentally ΔV values for the solid solutions.

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