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# Phase Transition of $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$, Anion Radical Salts. Thermodynamical Stability of the Solid Solutions

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**Synopsis.** The phase transition and the thermodynamic properties of solid solutions were studied with anion radical salts of $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$. The stability condition of the solid solutions was examined in both the low- and high-temperature phases.

Much attention has been paid to solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) because of their prominent electronic properties.[1–12] In particular, the anion radical salt of methyltriphenylphosphonium, $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, undergoes a solid-state phase transition at 315.7 K.[1–8] The methyltriphenylarsonium salt, $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, although it exhibits electronic properties very similar to those of the phosphonium salt, shows no such phase transition up to the decomposition temperature at 1 atm pressure.[1–3,6–11] Moreover, one can prepare the salts containing the mixed cations represented by $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$.[1,2,6–11] The phase transitions of these mixed anion radical salts have been studied, as a function of the composition parameter, by observing anomalies in the temperature dependence of the static magnetic susceptibilities and the electrical conductivities and also by means of thermal analyses.[2,6–8] The experimental relation between the transition temperature and the composition parameter ($x$) at 1 atm pressure is illustrated in Curve (a) of Fig. 1. In order to understand the thermodynamic behavior of the phase transitions against the composition parameter, we proposed in a previous paper a thermodynamical theory of binary regular solid solution model for those TCNQ mixed crystals.[11] In the present paper, we shall examine the condition of the thermodynamical stability of the solid solutions and investigate the mechanism of the phase transitions.

According to the previous paper,[11] a thermodynamical theory of binary regular solid solution model is applicable to $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$. This model assumes an ideal mixing of the two components of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, ($x$=0.00), and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, ($x$=1.00), because the crystal structure and the chemical properties of the phosphonium salt are very similar to those of the arsonium salt. The model further assumes that the phase transition of a solid solution does not change the manner of ideal mixing of the two components. In this respect, it is important to note that the phase transition of our system is not the usual order-disorder type with respect to the mixing of the two components. Moreover, we could well assign the low- and high-temperature phases of the solid solutions at 1 atm pressure as $\alpha\gamma$ and $\beta\gamma$ phases, respectively.[9–11] Their Gibbs free energies per mol were expressed by

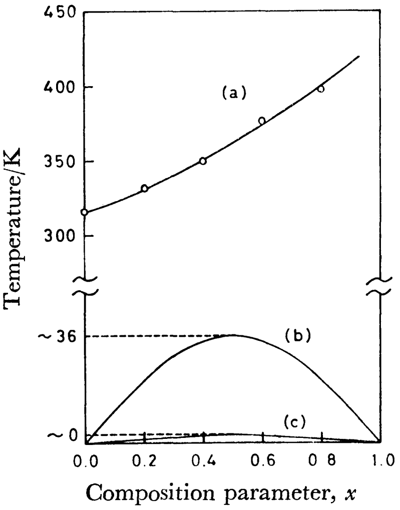

Fig. 1. Curve (a) shows the experimental relation between the temperature of the $\alpha\gamma \rightarrow \beta\gamma$ phase transition and the composition parameter ($x$) of the solid solutions of $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\dot{-}}$, $(0 \leq x \leq 1)$, anion radical salts at 1 atm pressure. Curves (b) and (c) show boundaries between the solid solution and the segregated region for the $\beta\gamma$ and $\alpha\gamma$ phases of the solid solutions, respectively. See text.

$$G^{i\gamma}(T,p,x) = (1-x)G_1^{i}(T,p) + xG_2^{\gamma}(T,p) + H_m^{i\gamma}(1-x)\cdot x + RT\{(1-x)\ln(1-x) + x\ln x\}, \quad (i=\alpha, \beta), \qquad (1)$$

where $T$ and $p$ represent temperature and pressure, respectively, and where $(1-x)$ and $x$ are the mole fractions of the component $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^{\dot{-}}$ and $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\dot{-}}$, respectively. $G_1^{\alpha}(T,p)$ and $G_1^{\beta}(T,p)$ are the Gibbs free energies per mol for the low-temperature ($\alpha$) and high-temperature ($\beta$) phases of pure phosphonium salt, respectively, while $G_2^{\gamma}(T,p)$ is that of the ($\gamma$) phase of pure arsonium salt at 1 atm pressure. $H_m^{i\gamma}$ is the heat of mixing per mol for each phase, and is assumed to be independent of temperature. The phase transitions of the solid solutions at 1 atm pressure can then be assigned to the $\alpha\gamma \rightarrow \beta\gamma$ process. By analyzing the experimental relation between the transition temperature of the $\alpha\gamma \rightarrow \beta\gamma$ phase transition and the composition parameter (Curve (a) of Fig. 1), we obtained the difference of the heat of mixing between the $\alpha\gamma$ and $\beta\gamma$ phases as $H_m^{\beta\gamma} - H_m^{\alpha\gamma} = 0.594 \pm 0.021$ kJ/mol.[11]

For either of the low-temperature ($\alpha\gamma$) or high-temperature ($\beta\gamma$) phase of our solid solutions, if the value of $H^{i\gamma}_{m}$, (i=$\alpha$ or $\beta$), is positive, the solid solutions are unstable below certain critical temperature and the segregation into the phosphonium salt and the arsonium salt should take place. It is well known that the theoretical relation between the mole fraction of the two components and the critical temperature at which the breaking of solid solution occurs can be determined by solving the equation

$$H_{m}{}^{i\gamma}(1-2x) + RT\ln\frac{x}{1-x} = 0. \qquad (2)$$

In the region above critical temperature the solid solutions are thermodynamically stable with ideal mixing of the two components, while the solid solutions do not exist below critical temperature. In the temperature region above $T^{i\gamma}_{m}=H^{i\gamma}_{m}/2R$, the solid solutions can be obtained with all compositions ranging from $x$=0.00 to $x$=1.00.

In the case of $[(C_6H_5)_3PCH_3]_{1-x}{}^{+}[(C_6H_5)_3AsCH_3]_{x}{}^{+}$ $(TCNQ)_2{}^{\cdot-}$, ($0\leq x\leq 1$), anion radical salts, although we have no information about the individual value of $H^{\alpha\gamma}_{m}$ or $H^{\beta\gamma}_{m}$, we can safely assume that the value of $H^{\alpha\gamma}_{m}$ may be very nearly equal to zero kJ/mol for the low-temperature ($\alpha\gamma$) phase, because the crystal and molecular structures of the $\alpha$ phase of the phosphonium salt are almost identical with those of the $\gamma$ phase of the arsonium salt.[12] Moreover, there acts no specific interaction between the methyltriphenylphosphonium and methyltriphenylarsonium cations in the $\alpha\gamma$ phase and the chemical properties of the phosphonium salt are very similar to those of the arsonium salt. The assumption of $H^{\alpha\gamma}_{m}\approx 0$ kJ/mol is also strongly supported by the reason to be mentioned in the following. Then, we have $H^{\beta\gamma}_{m}\approx 0.594$ kJ/mol for the high-temperature ($\beta\gamma$) phase of the solid solutions. This positive $H^{\beta\gamma}_{m}$ value is reasonable, because the molecular and crystal structures of the $\beta$ phase of the phosphonium salt are closely related to those of the $\gamma$ phase of the arsonium salt but a difference was found in the conformation of the methyltriphenylphosphonium cation with respect to the intramolecular rotation of the phenyl groups.[12]

First, we neglect the effect of the $\alpha\gamma\rightarrow\beta\gamma$ phase transition, and only consider the $\beta\gamma$ phase of the solid solutions. By the use of $H^{\beta\gamma}_{m}\approx 0.594$ kJ/mol, together with Eq. 2, the boundary between the solid solutions and the segregated region is obtained as shown in Curve (b) of Fig. 1. In the region above Curve (b) the solid solutions composed of ideally mixed $\beta$ form of the phosphonium salt and the $\gamma$ form of the arsonium salt are stable, while they have to be segregated into two components below Curve (b). $T^{\beta\gamma}_{m}$ at $x$=0.50 is calculated to be about 36 K.

In view of these results, we can understand the importance of the $\beta\gamma\rightarrow\alpha\gamma$ phase transitions (Curve (a) of Fig. 1) of the solid solutions. If there were no such phase change, the $\beta\gamma$ phase would become unstable in going to low temperatures and the crystals of the solid solutions would break. Actually, however, the solid solutions change into the $\alpha\gamma$ phase at Curve (a) of Fig. 1, which lies in the temperature region much higher than does Curve (b) of Fig. 1. As for the $\alpha\gamma$ phase, since $H^{\alpha\gamma}_{m}\approx 0$ kJ/mol and thus $T^{\alpha\gamma}_{m}\approx 0$ K, the boundary between the solid solutions and the segregated region is schematically given by Curve (c) of Fig. 1, that is, the solid solutions composed of the $\alpha$ form of the phosphonium salt and the $\gamma$ form of the arsonium salt will be stable down to 0 K in all compositions. This prediction may be supported by the experimental results by Kosaki *et al.*[8] For example, the fact that the observed heat capacity *versus* temperature curve of the $\alpha\gamma$ phase of the solid solution with the composition $x$=0.449 is smooth down to about 10 K means that the solid solution does not break and that the $\alpha\gamma$ phase is stable at least down to 10 K. This experimental result also implies very small value (less than 0.17 kJ/mol) for $H^{\alpha\gamma}_{m}$ in the $\alpha\gamma$ phase.

Our investigation clearly shows that, because of the $\beta\gamma\rightarrow\alpha\gamma$ phase transition, the solid solutions of $[(C_6H_5)_3PCH_3]_{1-x}{}^{+}$ $[(C_6H_5)_3AsCH_3]_{x}{}^{+}$ $(TCNQ)_2{}^{\cdot-}$,($0\leq x\leq 1$), anion radical salts are stable both in the temperature range from 0 K up to decomposition temperatures and in the whole composition range from $x$=0.00 to $x$=1.00. So far, this conclusion agrees well with the experimental observations.[1-8] Another important conclusion is concerned with the mechanism of the phase transition of the solid solutions. The existence of the $\beta\gamma\rightarrow\alpha\gamma$ phase change is necessary to avoid breaking of the $\beta\gamma$ phase at low temperatures.

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