

The Phase Transitions of the Anion Radical Salts Containing Mixed Cations; $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$)

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The phase transitions of the anion radical salts containing mixed cations represented by $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$) were investigated. The transition temperature, T_c , and the magnitude of the heat, ΔH , of the transition were determined as a function of the composition parameter, x , by means of a differential scanning calorimeter. It was found that T_c increases, and ΔH decreases, monotonously with an increase in the value of x , and that the phase transition disappears with $x=1.00$. The mechanism of the phase transitions was discussed on the basis of the theory of triplet exciton-exciton interaction proposed by Chesnut. The theoretical values of the entropy changes of the transitions were found to be much less than those observed. In view of these results, it was concluded that the anomalies in the magnetic susceptibilities of these salts were induced by the change in the crystal structure.

There are a few ion-radical salts that are known to undergo phase transitions.¹⁻⁷ The phase transitions of such ion-radical salts are particularly interesting, because the anomalies in the magnetic susceptibilities are associated with the phase transitions.¹⁻⁶

Much attention has been paid to the solid anion-radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ).^{5,6,8-10} In the course of our study of these salts, we found that the ESR absorption intensity, which is proportional to the paramagnetic susceptibility, of the salt of methyltriphenylphosphonium, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, increases abruptly at 40°C when the temperature is raised.⁶ This discontinuity was also found in the electrical conductivity at that temperature.⁶ This anomaly was ascribed to the phase transition of the crystal, as evidenced by the differential thermal analysis.¹¹ The methyltriphenylarsonium salt, $[(C_6H_5)_3AsCH_3]^+(TCNQ)_2^-$, exhibits electronic properties almost

identical with those of the phosphonium salt; on the other hand, the arsonium salt is known to have no such anomaly. One can prepare the salts containing mixed cations, which may be expressed as $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$).^{5,6} Therefore, it seemed that it would be interesting to investigate the effect of the composition upon the phase-transition phenomenon. The present investigation was performed by means of a differential scanning calorimeter (DSC).

An attempt has previously been made to explain the mechanism of the phase transitions of ion-radical salts in terms of the cooperative spin-exchange interaction.¹² Hence, the experimental results of our DSC measurements will be discussed in terms of such a theoretical consideration. In other words, we shall examine to what extent the spin-exchange interaction of these TCNQ anion radical salts contributes to the phase transition mechanism. Knowledge as to the effect of the chemical composition upon the phase transition is useful for this purpose.

The present study has already been reported in part in a short communication.¹³

Experimental

Materials. The preparation of TCNQ has been described by Acker and Hertler.¹⁴ It was purified by recrystallization from acetonitrile. The anion-radical salts containing the mixed cations, $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$), were synthesized according to the method of Melby *et al.*⁸ The six salts were prepared with compositions of $x=0.00$,

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0.20, 0.40, 0.60, 0.80, and 1.00.

Hexachloroethane (Wako Pure Chemical Industries, Ltd., GR grade) was used without further purification. Hexamethylbenzene (Eastman Kodak Co., white-label grade) was purified by recrystallization from ethanol.

Measurements. The DSC measurements were performed by means of a Rigakudenki Thermoflex apparatus. The rate of raising the temperature was 3.0°C/min. As a reference, powdered α -alumina was employed. The sample and the reference were packed and sealed, respectively, into aluminium vessels in order to prevent weight loss due to the sublimation. In DSC measurements, the peak area of the signal line should be proportional to the magnitude of the heat, ΔH , associated with the phase transition. Therefore, in order to determine the heat of transition, the integrated area of the peak of $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$ was compared with that of hexachloroethane or hexamethylbenzene. The phase transition of hexachloroethane is known to take place at 318.1°K with $\Delta H=0.613$ kcal/mol and at 344.4°K with $\Delta H=1.965$ kcal/mol,^{*1} and that of hexamethylbenzene, at 384.1°K with $\Delta H=0.42$ kcal/mol.¹⁵⁾ In this technique, it was necessary to employ standard materials whose transition temperatures were close to those under investigation.

Results

In $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, where $0 \leq x \leq 1$, all the salts except for that with $x=1.00$ were found to show phase transitions. For instance, one of the DSC thermograms for $[(C_6H_5)_3PCH_3]_{0.80}^+[(C_6H_5)_3AsCH_3]_{0.20}^+(TCNQ)_2^-$ is reproduced in Fig. 1. These phase transitions were endothermic when the temperature was raised, and reversible when the temperature was lowered. The transition temperature, T_c , and the magnitude

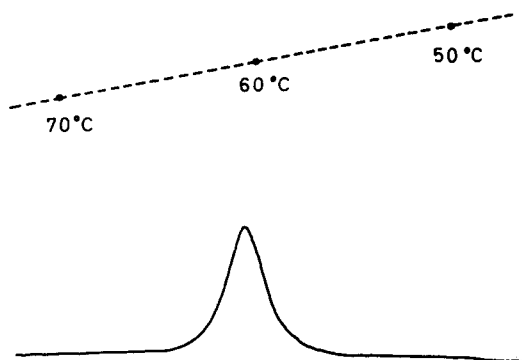


Fig. 1. One of the DSC thermograms for $[(C_6H_5)_3PCH_3]_{0.80}^+[(C_6H_5)_3AsCH_3]_{0.20}^+(TCNQ)_2^-$. The rate of raising temperature was 3.0°C/min.

of the heat, ΔH , associated with the phase transitions of these salts are listed in Table 1, together with the molecular weight, the sample weight used for this experiment, and the heat of transition of the specimen. On the basis of these results, the relations of T_c and of ΔH to the composition parameter, x , are illustrated in Fig. 2.

In the salt of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, where $x=0.00$, the values of $T_c=41.5^\circ\text{C}$ and $\Delta H=4.5 \times 10^2$ cal/mol were obtained from these DSC measurements. These values were in agreement with the values, $T_c=315.7^\circ\text{K}$ and $\Delta H=487$ cal/mol respectively, which were obtained from the heat-capacity measurement by Kosaki *et al.*¹⁶⁾

As is shown in Fig. 2, it was found that, in the salts where $0 < x < 1$, T_c increases and the value of ΔH decreases, monotonously with an increase in the value of x , and that the phase transition

TABLE I. THE DATA ON THE TRANSITION TEMPERATURE, T_c , AND THE HEAT, ΔH , ASSOCIATED WITH THE PHASE TRANSITION IN $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$)*

Composition parameter x	Molecular weight	Sample weight (mg)	T_c ($^\circ\text{C}$)	ΔH^{**} (cal/s.w.)	ΔH (cal/mol)
0.00	685.70	26.6	41.5	1.7×10^{-2}	4.5×10^2
0.20	694.49	29.8	59.0	1.9×10^{-2}	4.4×10^2
0.40	703.28	32.0	76.3	1.6×10^{-2}	3.5×10^2
0.60	721.07	26.2	103.0	9.2×10^{-3}	2.5×10^2
0.80	720.86	29.2	124.3	4.3×10^{-3}	1.1×10^2
1.00	729.65	24.9	—	0	0

* The data on the molecular weight, the sample weight used for this DSC measurement and the heat of transition per the sample weight are also given.

** The value of the heat of transition per the sample weight.

*1 We should keep in mind that hexachloroethane is somewhat volatile. However, although this material, when packed and sealed into the aluminium vessel, was heated up to about 350°K at the rate of 3.0°C/min, the weight loss due to the sublimation was found to be less than 0.5%.

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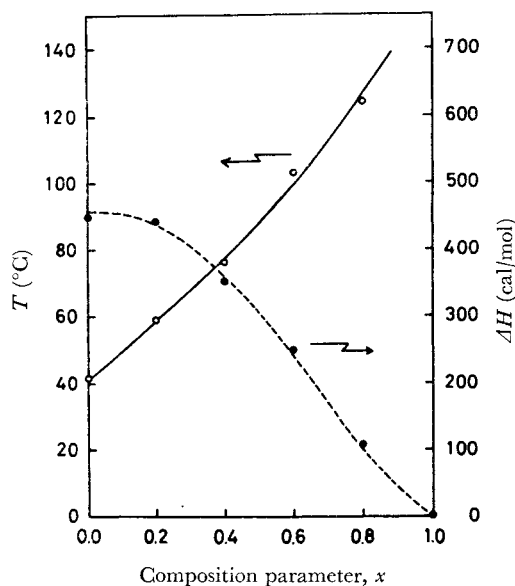


Fig. 2. The relations of the transition temperature, T_c , and of the magnitude of the heat, ΔH , associated with the phase transition, to the composition parameter, x , in $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+ (TCNQ)_2^-$, ($0 \leq x \leq 1$).

disappears at $x=1.00$. We can see that T_c is raised almost linearly as the value of x increases. On the other hand, the value of ΔH decreases slowly as the value of x increases in the region where $0 \leq x \leq 0.4$, while it decreases almost linearly as the value of x increases in the region where $0.4 \leq x \leq 1.0$. When $x \approx 1.00$, T_c may be extrapolated to about $160^\circ C$, although the value of ΔH tends towards zero.

Discussion

Triplet Exciton Interaction. These TCNQ anion-radical salts are composed of diamagnetic cations, TCNQ anion-radicals, and formally neutral TCNQ molecules. If the spins associated with the TCNQ anion-radicals did not interact, the magnetic susceptibility of these compounds would follow the Curie law. However, the magnetic susceptibility measurements have shown that this is not the case.⁵⁾ The extra electrons on the TCNQ molecules appear to be paired by an exchange interaction. These systems are known to contain a singlet ground state and a triplet exciton state. The TCNQ molecules are believed to be arranged in plate-like fashion in a unique crystal direction.^{5,9)}

In order to account for the occurrence of the phase transitions of these anion-radical salts, a simple phenomenological model has been proposed by Chesnut.¹²⁾ He showed that a certain type of order-disorder transition with respect to triplet excitation density does occur if one includes in the interaction a term which is quadratic in the triplet

excitation density, ρ . In this case, the free energy, A , and the entropy, S , of the system for the N anions are represented by:

$$A = \frac{1}{2}N \left[\epsilon_0 \rho + \frac{1}{2} \epsilon_1 \rho^2 - kT \left\{ \rho \ln g - \rho \ln \rho - (1-\rho) \ln (1-\rho) \right\} \right], \quad (1)$$

$$S = \frac{1}{2}Nk \left\{ \rho \ln g - \rho \ln \rho - (1-\rho) \ln (1-\rho) \right\}, \quad (2)$$

where g is the multiplicity ($g=3$ for the triplet state), where ϵ_0 is the singlet-triplet energy separation, and where ϵ_1 is the interaction energy due to triplet exciton-exciton interaction.

The equilibrium value of ρ may be found by minimizing A with respect to ρ . The phase transition will take place at the temperature where two equally stable minima occur. In this case, the transition is of the first order. The spin entropy change will be:

$$\Delta S_{\text{spin}} = \frac{1}{2}R\Delta\rho \ln g, \quad (3)$$

where $\Delta\rho$ is the change in the triplet excitation density at the transition. $\Delta\rho$ can be calculated from the magnetic susceptibility data, since an abrupt change in the paramagnetic susceptibility at the transition temperature is due to the change in the triplet exciton population, $\Delta\rho$. Therefore, one can evaluate the magnitude of the spin entropy change by means of Eq. (3).

Comparison with Experimental Results.

Kepler found a sharp discontinuity in the temperature variation of magnetic susceptibility in the crystals of $[(C_6H_5)_3PCH_3]_{1-x}^+ [(C_6H_5)_3AsCH_3]_x^+ (TCNQ)_2^-$, except for the salt with $x=1.00$.⁵⁾ At the temperature where the discontinuity occurred, there was an abrupt increase in the magnetic susceptibility in the higher temperature range. This critical temperature shifts to higher temperatures as the value of x increases. This relation is in good accordance with that obtained from the DSC measurements.

The values of $\Delta\rho$ were calculated from Kepler's susceptibility data. For example, in $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, where $x=0.00$, $\Delta\rho=0.12$ is centered about the point where $\rho=0.37$. This leads, by Eq. (3), to; $\Delta S_{\text{spin}}=0.13$ cal/deg·mol. Similar calculations were made for the mixed crystals. Thus, the relation of ΔS_{spin} to x was found to be as shown in Fig. 3.

On the other hand, the observed entropy changes, ΔS_{obs} , at the transition were evaluated from the observed values of T_c and ΔH . The relation of ΔS_{obs} to x is also illustrated in Fig. 3.

As is shown in Fig. 3, it was found that the values of ΔS_{spin} were much less than those of ΔS_{obs} for all of the compounds. For example, in $[(C_6H_5)_3-$

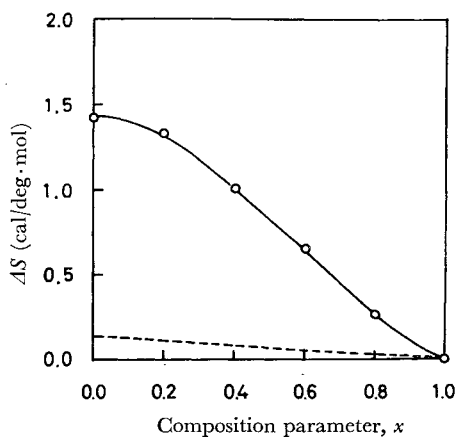


Fig. 3. The relation of the entropy change at the phase transition to the composition parameter, x , in $[(C_6H_5)_3PCH_3]_{1-x}[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, ($0 \leq x \leq 1$). ΔS_{obs} (the solid line) represents the total entropy change estimated from the observed values of ΔH and T_c in Fig. 2. ΔS_{spin} (the dotted line) represents the spin entropy change calculated from the Chesnut's theory by Eq. (3).

$PCH_3]^+(TCNQ)_2^-$, $\Delta S_{spin} = 0.13$ cal/deg·mol, while $\Delta S_{obs} = 1.4$ cal/deg·mol. Therefore, the value of ΔS_{spin} is as small as 9.1% of that of ΔS_{obs} . Although the values of both ΔS_{spin} and ΔS_{obs} decrease with an increase in x , the ratio of ΔS_{spin} to ΔS_{obs} remains nearly constant in the mixed crystals.

Conclusion

The above-mentioned results clearly indicate that the total entropy change can not be understood solely by the spin-entropy change calculated from Chesnut's theory. This means that it is hopeless to consider only the spin system as the source of

entropy creation at the transition. Therefore, one must also take into consideration the entropy change due to the change in the crystal structure. In this case, the magnitude of this entropy change reaches about 90% of the observed total entropy change. This kind of entropy change decreases as the percentage of the methyltriphenylarsonium cation of the salt increases. Since, in these TCNQ anion-radical salts, the crystal structure above the transition temperature is expected to be appreciably different from that below the transition temperature, it is desirable to study the difference in these crystal structures by X-ray analysis.*² The anomalies in the magnetic susceptibilities of these anion-radical salts are probably induced by the change in the crystal structures.

*² There are some other ion-radical salts that undergo phase transitions. It is well known that the phase transition of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (Würster's Blue) perchlorate, one of the stable cation-radical salts, takes place at 189°K. Elliot and Wolfsberg,¹ Duffy,² and Okumura³ found a sharp decrease in the paramagnetic susceptibility below this transition temperature, where Würster's Blue cations are known to pair up to form dimers with a ground singlet state and an excited triplet state.⁴ If Chesnut's theory is applied to this transition, Okumura's susceptibility data indicate that $\Delta\rho = 0.087$ symmetrically about $\rho = 0.643$. This leads by Eq. (3) to: $\Delta S_{spin} = 0.095$ cal/deg·mol. This value is much less than the value, $\Delta S_{obs} = 2.19 \pm 0.02$ cal/deg·mol, which was obtained from the heat-capacity measurements by Chihara *et al.*⁷ They said that it was difficult to consider only the spin system as the source of entropy creation at the transition.⁷ Again, in this salt, the rest of the entropy must then come from some structural changes. In fact, X-ray diffraction studies, cited by McConnell,⁴ show that the transition is accompanied by a small structural change from the room-temperature orthorhombic phase to the low-temperature monoclinic phase. These results seem to be, in some respects, very similar to those for the present TCNQ anion-radical salts.