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The Phase Transitions of the Anion Radical Salts of $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^-$, $(0 \leq x \leq 1)$, as Studied by the ESR Measurements

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The prominent magnetic, electrical, and optical properties of the solid anion radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) have been the subject of many theoretical and experimental investigations over the past several years.[1–11] In particular, the anion radical salts containing the mixed cations represented by $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^-$, $(0 \leq x \leq 1)$, show electron spin resonance (ESR) spectra characteristic of a triplet exciton state lying close to a singlet ground state.[1,3,11]

The salt of $[(C_6H_5)_3PCH_3]^+(TCNQ)^-$, $(x=0.00)$, undergoes a first-order phase transition at 315.7 K, where we earlier found anomalies in the temperature dependences of the ESR absorption and the electrical conductivity,[6,9] while the salt of $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^-$, $(x=1.00)$, does not undergo such a phase transition.[5,8,10] The phase transitions of the anion radical salts containing the mixed cations have been studied, as a function of the composition parameter, by means of a differential scanning calorimeter (DSC) and by observing the anomalies in the temperature dependences of the magnetic susceptibility and the electrical conductivity.[5,8,10] The purpose of the present paper is to show that the measurements of the ESR absorption and its variation with the temperature are useful for investigating the phase transitions of these mixed crystals.

The six anion radical salts with the compositions of $x=0.00$, 0.20, 0.40, 0.60, 0.80, and 1.00 were prepared according to the method of Melby *et al.*[2] The ESR spectra of single crystals (5 mm × 5 mm × 1 mm) in the temperature range including the transition temperature were measured by means of a JES-ME X-band spectrometer with 100 KHz modulation. The temperature of the specimen was controlled to within ±1°C by its temperature equipment.

The ESR spectra of the triplet excitons in $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^-$, $(0 \leq x \leq 1)$, have been shown from the anisotropic zero-field splitting at low temperatures.[1,3,11] Until the transition temperature, as the temperature is raised, the doublet components due to the zero-field splitting in the ESR spectra broaden and move together, eventually collapsing into a single line which becomes progressively sharper, while the temperature dependence of the ESR absorption intensity can be understood in terms of an equilibrium between a singlet ground state and a triplet state lying an energy (0.065 eV) above the ground state; this system has been established by Kepler from the temperature dependence of the static magnetic susceptibility.[5] However, striking discontinuities in the temperature dependence of the ESR spectra were found for all the salts except for that with $x=1.00$. At the temperature where the anomaly occurs, the linewidth of the ESR absorption becomes abruptly sharper, while the intensity discontinuously increases, in the higher temperature range. This change was found to be thermally reversible. In the region above this temperature, the linewidth is practically constant, while the intensity gradually decreases, as the temperature is raised.

As an example, the salt of $[(C_6H_5)_3PCH_3]_{0.80}^+$ $[(C_6H_5)_3AsCH_3]_{0.20}^+$ $(TCNQ)_2^-$, $(x=0.20)$, is described in some detail. At 59±1°C where the anomaly occurs, the ESR spectra of a single crystal for an arbitrary orientation were recorded just below and above this temperature, as is shown in Fig. 1. These spectra were obtained with the same spectrometer gain settings. In this salt, the intensity of the ESR absorption increased abruptly by a factor of about 1.2 in the

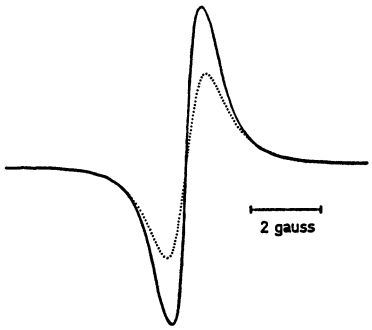

Fig. 1. The ESR spectra of a single crystal of $[(C_6H_5)_3PCH_3]_{0.80}^+[(C_6H_5)_3AsCH_3]_{0.20}^+(TCNQ)_2^-$, $(x=0.20)$, for an arbitrary orientation at 59±1°C, where a discontinuity occurs in the temperature dependence of the ESR absorption. The solid line and the broken line are the ESR spectra recorded just above and below this temperature, respectively, with the same spectrometer gain settings.

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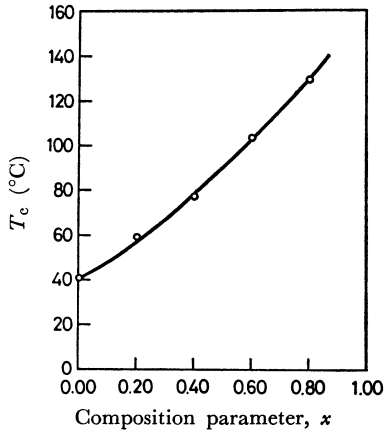

Fig. 2. The relation of the temperature, T_c, where the anomaly occurred in the temperature dependence of the ESR absorption, to the composition parameter, x, in $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\overline{\cdot}}$, $(0 \leq x \leq 1)$.

higher-temperature range. Although the linewidth was found to be somewhat anisotropic, for a fixed orientation the linewidth of 1.1_2 gauss in the lower-temperature range abruptly sharpened to 0.8_4 gauss in the higher-temperature range.

In $[(C_6H_5)_3PCH_3]_{1-x}^+[(C_6H_5)_3AsCH_3]_x^+(TCNQ)_2^{\overline{\cdot}}$, $(0 \leq x \leq 1)$, the temperature, T_c, at which the anomaly occurred in the ESR spectra shifts progressively to higher temperatures as the value of the composition parameter, x, is increased. The relation of T_c to x was obtained as is illustrated in Fig. 2. This relation was found to be in good accordance with the relation of the phase-transition temperature to the composition parameter, as has been determined previously from the DSC measurements or from the electrical conductivity measurements.[8,10] On the other hand, the magnitude of the discontinuity of the ESR absorption intensity at T_c was found to decrease gradually as the value of x increased. This situation was good agreement with that investigated on the basis of static magnetic susceptibility measurements by Kepler.[5] However, in the salt of $[(C_6H_5)_3AsCH_3]^+$ $(TCNQ)_2^{\overline{\cdot}}$, $(x=1.00)$, no discontinuity in the temperature dependence of the ESR absorption was observed up to about 150°C.

At the transition temperature, the increase in the ESR absorption intensity and the decrease in the linewidth in the higher-temperature range can be understood by assuming that the abrupt reduction in the singlet-triplet energy separation is caused by the phase transition in the higher-temperature range.[12] In this case, at the transition temperature the ESR absorption will be markedly intensified in the higher-temperature range because the population of the paramagnetic triplet excitons is abruptly increased by the reduction of the singlet-triplet energy separation. Since the linewidth of the ESR absorption is narrowed by the exchange interaction due to the triplet exciton collisions,[3] the abrupt increase in the exciton population gives rise to a sharper linewidth of the ESR absorption in the higher-temperature range.

In view of these results, the application of the ESR absorption and its variation with the temperature brings valuable knowledge concerning the phase transitions of the $[(C_6H_5)_3PCH_3]_{1-x}^+$ $[(C_6H_5)_3AsCH_3]_x^+$ $(TCNQ)_2^{\overline{\cdot}}$, $(0 \leq x \leq 1)$, anion radical salts.

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