The Heat Capacity and the Phase Transition of the $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^-$ Crystal

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The measurements of the temperature dependence of the magnetic susceptibility as well as the intensity of ESR spectra[1] of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^-$ crystals have already revealed that there is some anomaly in their curves at around 40°C. The magnetic behavior has been explained in terms of a siglet - triplet transition based on the correlation between the electronic spins of each molecule, and the anomaly has been referred to a discontinuous change in the correlation energy at this temperature. The pressure dependence of the anomalous point has also been investigated by McConnell *et al.*[2] No consistent interpretation for the mechanism of this anomaly has, however, yet been given. The purpose of the present investigation is to measure the heat capacities of this radical salt precisely in order to clarify the mechanism of this anomaly.

This radical[3] was prepared by means of $(C_6H_5)_3P$ CH_3I and TCNQ (tetracyanoquinondimethan). The phosphonium salt and TCNQ were dissolved separately into acetonitrile and then mixed at about 70°C. This mixture was allowed to stand for about one day to produce black prism crystals as precipitates.

The heat capacities were measured with an adiabatic calorimeter[4] in the temperature region from 11 to 350°K.

As is shown in the following figure, the heat-capacity curve exhibited a phase transition at

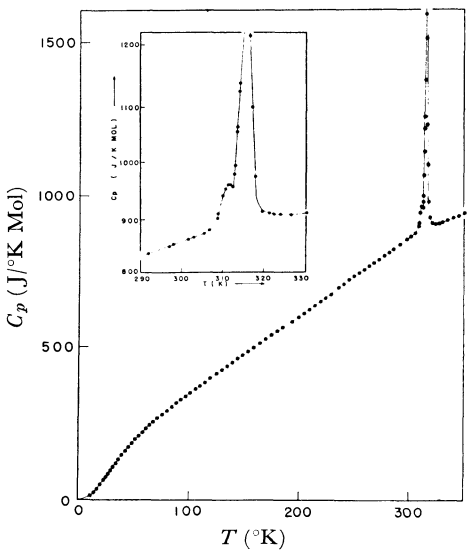

Fig. 1. Heat Capacity of $[(C_6H_5)_3PCH_3]^+$ $(TCNQ)_2^-$.

315.7°K. The enthalpy and the entropy of transition were found to be 2030.0 J mol^{-1} and 7.1989 J°K^{-1} mol^{-1} respectively. This amount of entropy cannot be explained solely by the freedom of electronic spins, as would be expected from the magnetic measurements. It may be added here that this transition is accompanied by a small hump, as is shown on an enlarged scale in the figure. In order to clarify the origin of this small anomaly as well as the mechanism of the phase transition, we are hereafter going to measure the dilution effect on the heat capacity of this compound of the formation of a series of solid solutions: $[(C_6H_5)_3PCH_3]_{1-x}^+$-$[(C_6H_5)_3As\,CH_3]_x^+(TCNQ)_2^-$, as the pure $[(C_6H_5)_3$-$As\,CH_3]^+$ $(TCNQ)_2^-$ compound has no transition point. The detailed data on these compounds will be reported in due course.

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