Anomalies in the Temperature Dependences of the ESR Absorption and Electrical Conductivity of an Anion Radical Salt, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$

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In recent years the anion radical salts of tetracyanoquinodimethane (TCNQ) have aroused much interest because of their prominent electronic properties. In particular, the magnetic property of the salts at low temperature range has been explained in full by Chesnut et al.[1,2] in terms of the singlet-triplet equilibrium resulting from the spin correlation between two anion radicals of TCNQ. Chesnut et al. have referred to the existence of a discontinuity in the magnetic susceptibility of the TCNQ salt of methyltriphenylphosphonium, $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, at 315°K.[1,3] In this report we will present the temperature dependences of the ESR absorption and electrical conductivity of the salt in the temperature range including 315°K.

Single crystals of the phosphonium salt were prepared in the manner described by Melby et al.,[4] and all the measurements were performed with these single crystals. The crystal showed the same ESR fine structures at about 130°K arising from the magnetic dipole interaction as has been examined by Chesnut and Phillips.[1] At a higher temperature range, where the fine structures coalesced, the ESR absorption intensity and the line width varied with the temperature, as shown in Figs. 1 and 2, respectively.

The intensity increased with the rising temperature until about 310°K, in accordance with the following equation:

$$\text{Intensity} \propto [kT(3+e^{J/kT})]^{-1} \quad (J=0.08\text{eV.}) \qquad (1)$$

A discontinuity in the intensity occurred at 310~315°K, and then the intensity seemed to obey Curie's law above 315°K. This means

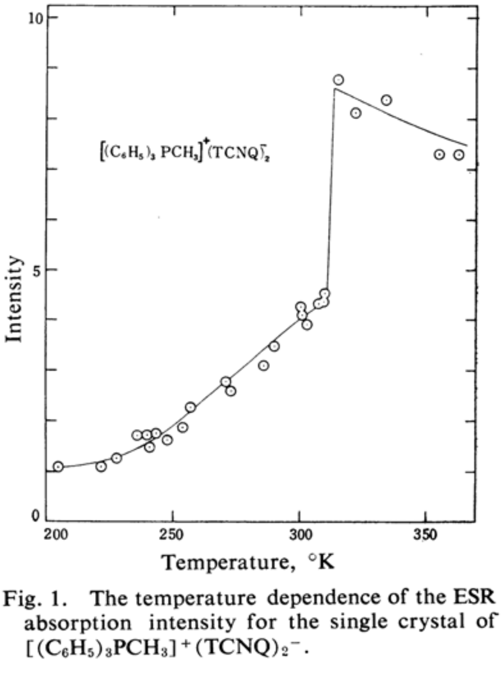

Fig. 1. The temperature dependence of the ESR absorption intensity for the single crystal of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$.

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[1] D. B. Chesnut and W. D. Phillips, *J. Chem. Phys.*, **35**, 1002 (1961).

[2] D. B. Chesnut and P. Arthur, Jr., ibid., **36**, 2969 (1962).

[3] M. T. Jones and D. B. Chesnut, ibid., **38**, 1311 (1963).

[4] L. R. Melby, R. J. Harder, W. R. Hertler, W. Mahler, R. E. Benson and W. E. Mochel, *J. Am. Chem. Soc.*, **84**, 3374 (1962).

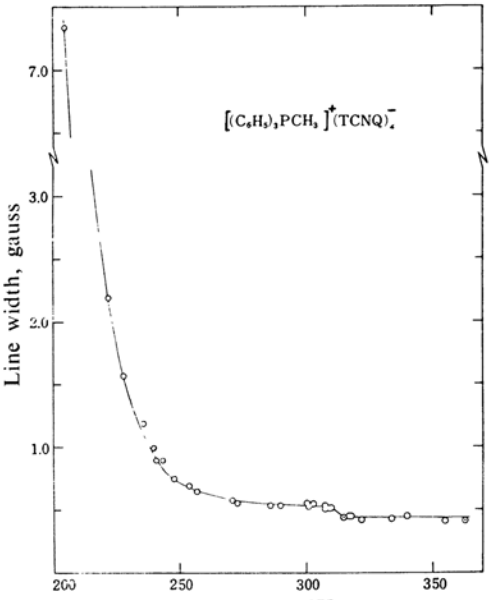

Fig. 2. The temperature dependence of the ESR absorption width (between the inflection points) for an arbitrary oriented single crystal of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$.

that the reduction of J in Eq. 1 should take place in the higher temperature range. The line width became slightly sharper above 315°K. These changes were found to be reversible. It is worthwhile noting that a similar anomaly has been found in the magnetic susceptibility of Würster's blue perchlorate at 186°K.⁵⁾

A similar discontinuity was found in the electrical conductivity, which was measured by the d. c. method. This is shown in Fig. 3. The crystal was a rectangular prism about 2×1×0.5 mm. The conductivity was measured in three directions, which were chosen arbitrarily so that (a) was along the long axis, (b) was normal to the largest plane, and (c) was perpendicular to (a) and (b). In all directions the conductivity varied abruptly by a factor of about 3.5 at about 310°K, and this change was reversible. The current varied with the applied voltage in good acordance with Ohm's law below the electric field of 100 V./cm., and it was found to be constant with time. Hence, the electronic conduction mechanism must be plausible for this salt. although in some salts, for example, $Li^+(TCNQ)^-$, the current was found to change with time; this may be attributable to a partial contribution from the ionic conduction. The activation energy E in the equation $\sigma=\sigma_0 \exp(-E/kT)$ was found to be almost isotropic, and its magnitude changed at the temperature where the anomaly occurred. These values were (a) 0.32 eV., (b) 0.29 eV. and (c) 0.30 eV. above 310°K, but a 0.42 eV., (b) 0.42 eV. and (c) 0.38 eV. below 310°K. On the other hand, the conductivity was not isotropic. This might be ascribed to anisotropy in the mobility of the charge carriers.

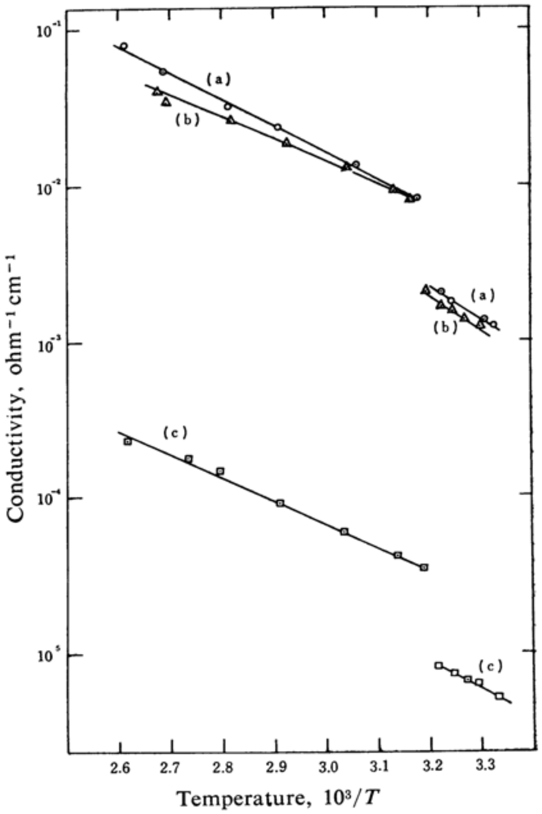

Fig. 3. The temperature dependence of the electrical conductivity of the single crystal of $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$, for three directions arbitrarily chosen (a), (b) and (c).

The reproducibility of our magnetical and electrical observations is good within the range of experimental error, and the values obtained did not depend on the specimens used. Hence, the discontinuity observed for the $[(C_6H_5)_3PCH_3]^+(TCNQ)_2^-$ crystal might be attributed to a phase transition, which is of the same type as has been suggested by McConnell and Lynden-Bell⁶⁾ for the case of the Würster's blue perchlorate crystal. Preliminary investigation by the X-ray diffraction method showed that there was a slight, but clear difference in the crystal lattices between those observed at temperatures below and above 310°K.

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5) W. Duffy, Jr., *J. Chem. Phys.*, **36**, 490 (1962).

6) H. M. McConnell and R. Lynden-Bell, ibid., **36**, 2393 (1962).