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Magneto-electrical studies of *p*-nitrophenol

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Abstract

The mean molar susceptibility (χ_M) as a function of temperature in the range $30 < T < 100$ °C has been measured for a powdered sample of *p*-nitrophenol, $NO_2C_6H_4OH$, (PNP). The electrical parameters of PNP, such as d.c. resistance, dielectric constant and pyroelectric current behaviour, have been measured accurately in the same temperature range for single crystals and polycrystalline powder. All these properties are interpreted in the light of the arrangement of the molecules in the unit cell as well as the structural phase change observed at 63°C.

INTRODUCTION

It is well known that crystalline *p*-nitrophenol, $NO_2C_6H_4OH$ (PNP), occurs in two forms, i.e. in two phases. The α form or low-temperature phase is stable below 63°C and the β form or high-temperature phase is stable above 63°C. The low-temperature phase undergoes a photochemical reaction, its colour changing from bright yellow to bright red, when illuminated with sunlight. The β form does not exhibit this property [1,2].

The crystal structures of the two phases have been determined [3–5]; the crystals are monoclinic and their parameters listed in Table 1.

The two forms are built of infinitely long chains in which the molecules are connected with hydrogen bonds of the type O–H · · · O. In the β form,

TABLE 1

X-ray data

Parameter	Phase I α form	Phase II β form
a (Å)	11.80	15.403
b (Å)	8.90	11.117
c (Å)	6.17	3.785
B (deg)	106° 52′	107° 04′
Space group	$P2_1/n$	$P2_1/a$

which does not change colour, the oxygen atoms of the NO_2 groups are located symmetrically with respect to the proton of the OH group of the preceeding molecule [3–5]; in the α form, one of the oxygen atoms lies slightly closer to the OH group than the other. According to Rohleder, this decreases considerably the potential barrier for the transition of the proton from the OH to the NO_2 of the next molecule in the α-*p*-nitrophenol crystals, which results in the formation of the quinoid structure and the colour of the crystal.

The magnetic anisotropy of the diamagnetic susceptibility of the α and β forms has been investigated [6]. In this paper we report on the electrical properties of the two forms. The mean molar susceptibility of the crystalline powder as a function of temperature has also been considered. All these parameters have been used to detect the structural phase change and also to determine whether or not the two forms are similar in their electrical properties.

EXPERIMENTAL

Large single crystals of α-*p*-nitrophenol were obtained (after two attempts) by evaporation of a saturated solution of purified α form in toluene at room temperature ($\approx 30\,^{\circ}C$).

For magnetic measurements, these crystals were ground to a very fine powder. The well known Gouy method was employed to measure the mean molar susceptibility, χ_M, in the temperature range $30 < T < 100\,^{\circ}C$.

Our electrical measurements were carried out on single crystals as well as on fine polycrystalline powder, obtained by grinding single crystals; the fine powder was pressed into pellets whose faces were coated with silver paste.

The d.c. resistance of single crystals and of the polycrystalline material was measured by means of a digital electrometer and a thermocouple with an accuracy of 1° C. The dielectric constant of PNP was obtained on an RLC digital bridge which was calibrated before the measurements using standard capacitors of 100 pf to 100 μf (decade condenser). The pyroelectric current was also studied using a digital picoammeter.

In all these measurements, three identical single crystals and three identical pellets were used. The results are reproducible for each measured parameter.

RESULTS AND DISCUSSION

The mean molar susceptibility, χ_M, of the polycrystalline powdered sample in the temperature range $30 < T < 100\,^{\circ}C$ is shown in Fig. 1. The sample is diamagnetic. The value of χ_M is nearly temperature-independent in the range $30 < T < 55\,^{\circ}C$. As the temperature approachs 60° C, a slight change in χ_M is observed and there is a broad peak centred at about

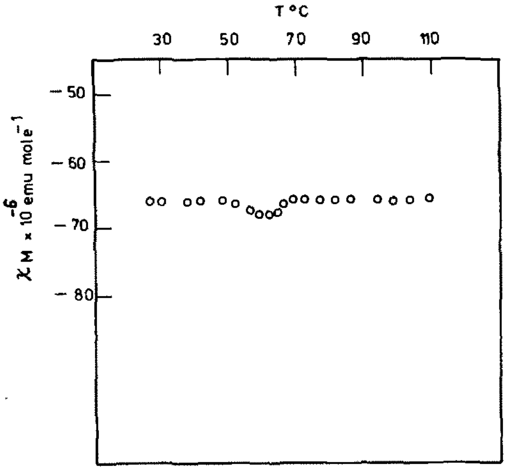

Fig. 1. Variation of the mean molar magnetic susceptibility, χ_M, with temperature, T ° C.

62–64° C. This anomalous behaviour in χ_M is taken as an indication of the structural phase change at $T \approx 63$° C.

All the electrical measurements on single crystals were carried out in such a way that the two electric poles were perpendicular to the needle direction.

Figure 2a and b) shows the relation between the resistance of the single crystals and the powdered samples as a function of temperature. It is easy to see that the sample is virtually a dielectric material. The variation of R with temperature is broadly similar, for both single crystals and powdered samples although the magnitude of R is different because it depends on the dimension of each sample. In the temperature range $30 < T < 50$ ° C, there is a rapid decrease in R as the temperature increases. In the temperature range $55 < T < 65$ ° C, there is a gradual increase in R as T increases. This results in a broad peak centred at 62–64° C which may be taken as indicating the structural phase transition. After the transition temperature, there is also a gradual decrease in R as the temperature increases, which means that the overall behaviour of the high-temperature form is broadly similar to that of the low temperature form, but with a lower resistance.

The behaviour of the resistance with temperature (and also that of the other electrical properties) can be explained with reference to the packing arrangement of the two structural modifications of the crystals [5].

Although the shortest intermolecular contacts are similar in the two modifications, the total number of short distances is about 25% higher in the α form, even though the densities of the two forms differ only by 1%: in the less dense β modification, there are 19 heavy atom contacts shorter than 3.6 Å, and 25 involving hydrogen atoms shorter than 3 Å, a total of 44; in the α-modification, there are 25 and 32 contacts of each respective size range, a total of 57. This difference is also reflected in the coordination numbers of the two structures: in the α form, every molecule makes contact with 30

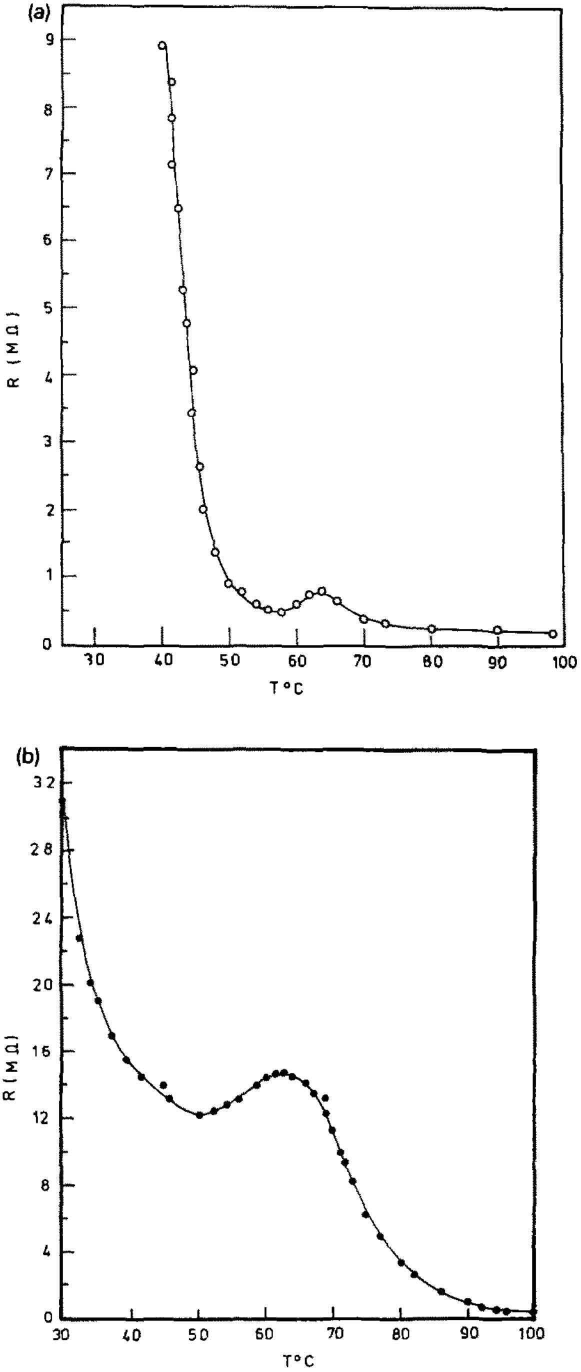

Fig. 2. a, Relation between the resistance, R, and the temperature, T ° C, of single crystals; b, Variation of the resistance, R, with temperature, T ° C, of polycrystalline material.

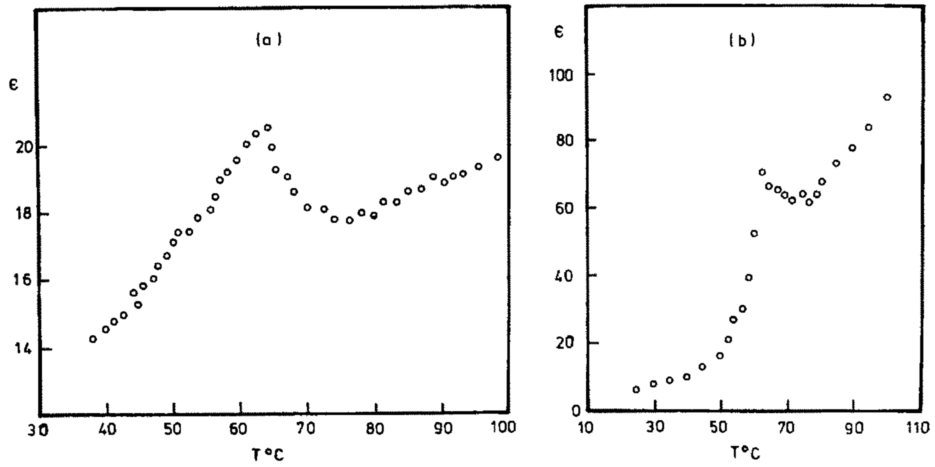

Fig. 3. Relationship between the dielectric constant, ε, and the temperature, T °C: a, single crystals; b, polycrystalline.

neighbouring molecules, while the β form has a coordination number of only 10. From the thermodynamic point of view, the structure with the higher coordination and the large number of intermolecular contacts is the more stable, as predicted by Kitaigorodskii's [7] close-packing theory.

It is clear from the preceeding analysis that the structure of the low-temperature form (α modification) is characterized by high coordination and a larger number of intermolecular contacts. In other words, at room (or lower) temperature, the molecules of the α form of PNP are closely packed which leads to a lower conductivity and, hence, a higher resistance than the less closely packed metastable β modification.

For the α modification (phase I), as the temperature increases (from room temperature) the packing arrangement decreases and hence the resistance also decreases. This is exactly the behaviour shown in Fig. 2a. When the temperature approaches around 63 °C, the thermal energy becomes sufficient to rearrange the molecules such that the number of shorter contacts becomes about 44 and the coordination number becomes 10 instead of 30: this structure is that of the β modification which is the metastable form of PNP.

Figure 3a shows the variation of the dielectric constant with temperature for single crystals of PNP. Figure 3b shows the same relation for the polycrystalline sample. The overall behaviour of ε with temperature is largely similar for the two samples. In the temperature range $30 < T < 60$ °C, there is a gradual increase in ε as the temperature increases, reaching a maximum value in the 62–64 °C range which corresponds to the structural phase change from the α modification to the metastable β modification of PNP. For phase II, as the temperature increases the value of ε increases. The

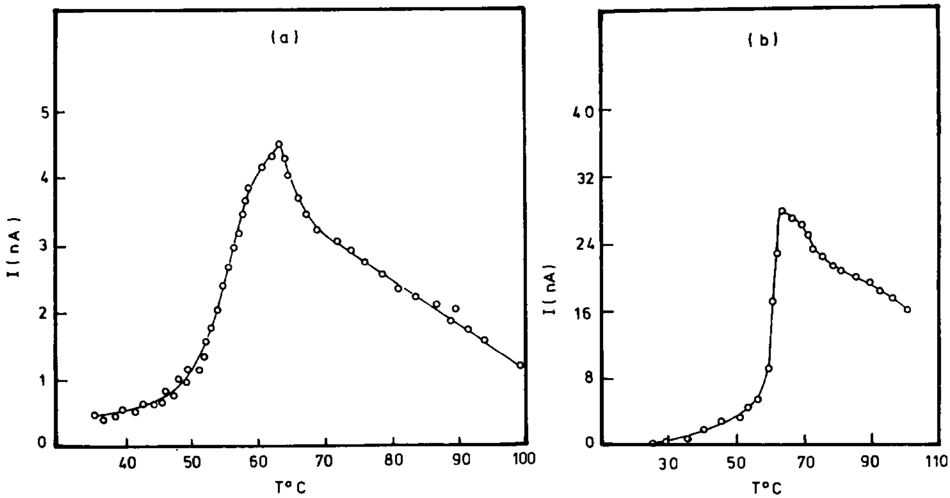

Fig. 4. Variation of the pyroelectric current, *I*, with temperature, *T* ° C: a, single crystals; b, polycrystalline.

behaviour of ε with *T* is as expected because it is nearly a mirror image of the behaviour *R*.

We have also studied the pyroelectric current behaviour: Fig. 4 shows its relationship with temperature for single crystals and polycrystalline materials. Again, as the temperature increases the value of the pyroelectric current increases, reaching its maximum value at about 63° C where the structural phase change of PNP takes place. This increase of *I* is followed by a decrease (after the transition temperature) as the temperature increases.

It can be concluded that all these physical properties support and confirm the structural phase change that has been observed in single crystals or polycrystalline PNP.

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