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Conduction in perylene–SbF₆[−], –PF₆[−] and –BF₄[−] complexes

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Abstract. Perylene (Per) was reacted with NO₂BF₄, NO₂PF₆, and NO₂SbF₆ in solid-solution reactions to produce solvent-free (Per)₂BF₄, (Per)₂PF₆, and (Per)₂SbF₆. X-ray diffraction identified the unit cells of the compounds as being orthorhombic in the first two cases and tetragonal in the last case. All of the compounds exhibited an increase in resistance with decreasing temperature indicative of a semiconducting type of behaviour and had room temperature resistivities of 700 Ω cm, 1.5 Ω cm, and 2.5 Ω cm, respectively. The conduction process has been analysed by fitting the data with a number of parameters in order to account for a nonlinearity in the $\ln \rho/\rho_0$ versus $1/T$ curves. The polaronic hopping model employed includes contributions of multiphonon processes, and intragrain and intergrain effects, and provides a good fit to the resistivity data as well as consistency with the results of Hall effect measurements.

1. Introduction

Perylene (C₂₀H₁₂) is a condensed ring hydrocarbon consisting of two naphthalene nuclei connected by two single bonds. In its pure form it is an insulator with a room temperature resistivity of 10¹³–10¹⁴ Ω cm [1, 2]. On cooling, the resistivity shows a typical semiconducting behaviour, increasing exponentially with decreasing temperature with an activation energy of approximately 1 eV [1, 2] according to

$$\rho \propto \exp(E_a/kT). \quad (1)$$

This molecule condenses in a monoclinic crystal cell with dimensions of $a = 11.27 \text{ \AA}$, $b = 10.82 \text{ \AA}$, $c = 10.26 \text{ \AA}$, $\beta = 100.55^\circ$ [3, 4]. There are four perylene molecules per unit cell and they are grouped in pairs with the planes of the molecules in each pair parallel and separated by 3.46 Å. Many different compounds and complexes have been created by interactions of a variety of molecules with perylene. For example, perylene acts as a donor when reacted with iodine [5–8] or bromine [9] and the resultant compounds are semiconductors with high conductivities. A hydrocarbon complex was formed when perylene was reacted with SbCl₅ in CCl₄ that was also semiconducting but with a changing activation energy [10]. This work stated that there was a sharp transition from a high-temperature regime with an activation energy of 0.098 eV above 210 K to a low-temperature regime below 210 K where the activation energy was 0.067 eV and that both of these regimes could be adequately described independently by the temperature dependence according to equation (1).

Keller *et al* [11] have previously prepared crystals of doped perylene from solution. Their products include Per₂(PF₆)_{1.1} × 0.8CH₂Cl₂, Per₂(PF₆)_{1.4} × 0.6THF, and Per₃(SbF₆)₂ × 0.75CH₂Cl₂. For the first two samples the dc conductivity parallel to the a -axis was of

the order of 10^2 – $10^3 \Omega^{-1} \text{ cm}^{-1}$ with a metallic behaviour between 300 K and 190 K and a semiconducting behaviour below 190 K. The conductivity in these materials is attributed to a mixed-valence state between the anions and the 'neutral' solvent molecules. As a result, the direct contribution of the anions to the conductivity in these materials cannot be fully realized. The x-ray diffraction results show that the PF_6^- -reacted samples are orthorhombic with the cell parameters of $a = 4.285 \text{ \AA}$, $b = 12.915 \text{ \AA}$, $c = 14.033 \text{ \AA}$, and $a = 4.26 \text{ \AA}$, $b = 12.79 \text{ \AA}$, $c = 13.89 \text{ \AA}$, respectively. The samples reacted with SbF_6^- were too small for physical investigation.

In this investigation perylene has been reacted with NO_2SbF_6 , NO_2PF_6 , and NO_2BF_4 in liquid SO_2 to produce organic compounds devoid of solvent molecules. With these molecules, the NO_2^+ ions act as an oxidizing agent for the perylene. The NO_2^+ is reduced to NO_2 gas which is pumped off with the solvent SO_2 via heating (40–50 °C) and a dynamic vacuum. The resulting compounds have been investigated by means of x-ray diffraction, temperature-dependent resistivity studies, and Hall effect measurements. Our goal was to determine the conductivity of this class of materials without having solvent molecules to facilitate a mixed-valence state. Also an attempt was made to explain the nature of the conduction process in these materials more completely by including a number of different parameters in the analysis of the conductivity data. Considerations have been made for multiphonon effects and both intragrain and intergrain conductivities. The conductivity has been analysed by various hopping mechanisms and the resulting data have been compared with other similar work.

2. Experimental details

Perylene (Aldrich, 99+%) was purified by sublimation under vacuum in a quartz tube at 175 to 200 °C. Commercially available nitronium hexafluoroantimonate, NO_2SbF_6 (Aldrich), was heated at 100–110 °C for three to four hours under dynamic vacuum. This process was needed to obtain a dry compound. In a typical reaction, purified perylene was allowed to react with the dried NO_2SbF_6 dissolved in liquid SO_2 in a double-ampoule reaction vessel. Reactions were carried out with perylene: NO_2SbF_6 molar ratios of 1:1, 2:1, and 3:1. There was excess unreacted NO_2SbF_6 with a ratio of 1:1 and there was insufficient NO_2SbF_6 with a ratio of 3:1 for a maximum SbF_6^- concentration in the compound. A 2:1 molar ratio provided a complete reaction with no excess NO_2SbF_6 . For this molar ratio an immediate reaction took place giving a purple solution and a solid. After stirring the reaction for 30 minutes, the purple coloration disappeared to give an orange solution and a greenish solid. The reaction was further stirred for 3–4 days without any change in appearance. A very dry greenish powder was obtained after the evaporation of SO_2 . The mass uptake of perylene corresponded to the formula $(\text{Per})_2\text{SbF}_6$ indicating that a complete reaction had taken place.

The reaction procedure for perylene with NO_2PF_6 (Aldrich, 99+%) was very similar to that described above. The NO_2PF_6 was heated under vacuum for 3 h at 100 °C to remove any hydrolysis product. A 2:1 molar ratio of perylene to dry NO_2PF_6 was reacted in SO_2 following the procedure described above. The solid/solution reaction produced a product that turned from reddish to black over 12 hours. On addition of SO_2 the product immediately turned purple and on stirring gave a black solid in a dark yellow solution. The final dry product after evaporation was black and had a mass uptake corresponding to $(\text{Per})_2\text{PF}_6$.

The NO_2BF_4 (Aldrich, 99+%) was dried under vacuum at 110 °C for 4–5 h to remove any hydrolysis product prior to reaction with perylene. The reaction took place under the same conditions as described above with a 2:1 molar ratio of perylene to NO_2BF_4 . After

standing for a few hours the solid mixture changed to a dark greenish/yellowish colour. On the addition of liquid SO_2 an intense yellow solution with a dark greenish solid was obtained. When the liquid was evaporated the dark greenish colour remained in the reacted solid. The mass uptake corresponded to a stoichiometry of $(Per)_2BF_4$.

A Nicolet powder diffractometer with $Cu K\alpha$ radiation was used for the x-ray powder diffraction measurements. The sample was placed under a thin, plastic wrap on a brass sample holder and was sealed in an inert atmosphere for all measurements. All of the measurements were performed at room temperature.

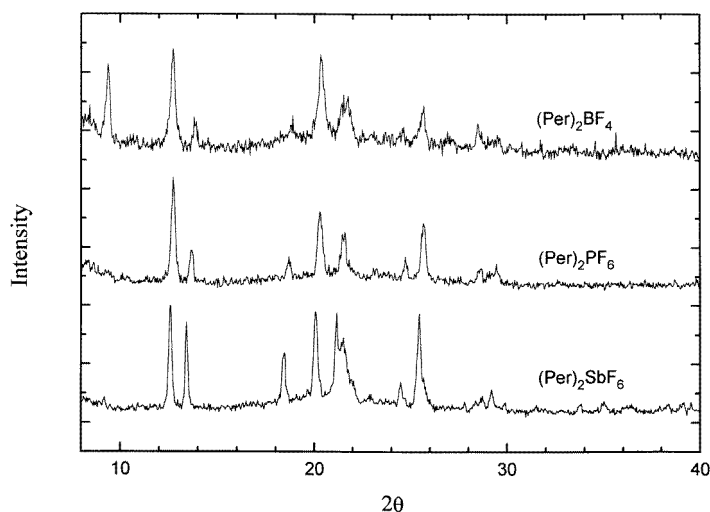


Figure 1. X-ray powder diffraction patterns of $(Per)_2BF_4$, $(Per)_2PF_6$, and $(Per)_2SbF_6$.

In order to facilitate resistivity and Hall effect measurements, electrical contacts were made with silver paste to pressed pellets of the reacted material. Contacts were set up for resistivity measurements in both the classical four-probe and van der Pauw methods [12], and in the Hall arrangement for the determination of the Hall coefficient. All samples were handled in an inert atmosphere and were sealed in a removable probe head with an indium o-ring to prevent exposure to air. For the Hall measurements the resistance detected by an offset of the voltage contacts in a direction parallel to the current direction was reduced by floating one of the voltage contacts with a potentiometer and by rotating the sample through 180° for each measurement to determine the odd component with respect to the field direction. This provided a resistance sensitivity between the Hall contacts of $\geq 0.01 \Omega$ with 1 mA of current through the sample. For the resistivity measurements the current direction was switched on each measurement and the voltage drops averaged. The resistivity measurements were performed between room temperature and 4.2 K in a cryostat cooled with both liquid N_2 and He with data taken during both cooling and warming cycles. The Hall effect was studied only at room temperature.

3. Results and analysis

The x-ray powder diffraction patterns of the reacted materials are shown in figure 1. A comparison of the observed and calculated 2θ -values from the fitting of the data for

Table 1. A comparison of observed x-ray diffraction peaks for (Per)₂SbF₆, (Per)₂PF₆, and (Per)₂BF₄ with those obtained by unit-cell fitting.

SbF ₆			PF ₆			BF ₄		
<i>hkl</i>	<i>2θ</i> observed	<i>2θ</i> fitted	<i>hkl</i>	<i>2θ</i> observed	<i>2θ</i> fitted	<i>hkl</i>	<i>2θ</i> observed	<i>2θ</i> fitted
300	12.571	12.588	200	12.711	12.658	110	9.413	9.410
102	13.410	13.413	020	13.647	13.660	200	12.740	12.748
312	18.420	18.434	220	18.664	18.665	020	13.889	13.840
113	20.066	20.066	310	20.238	20.242	121	18.762	18.767
402	21.157	21.146	102	21.426	21.435	310	20.397	20.353
510	21.464	21.478	031	22.992	22.989	002	21.717	21.715
412	21.599	21.566	022	24.693	24.684	230	24.550	24.597
431	22.030	22.016	321	25.668	25.676	400	25.640	25.658
422	22.801	22.783						
330	28.499	28.492						
323	24.486	24.506						
432	24.681	24.684						
531	25.439	25.439						
004	26.638	25.633						
610	25.727	25.686						
541	27.816	27.829						
630	28.395	28.380						
612	28.747	28.768						

the reacted samples is shown in table 1. The fit provides a tetragonal unit cell for the SbF₆⁻-reacted compound and orthorhombic unit cells for the other two compounds with dimensions of $a = 21.079 \text{ \AA}$, $b = 21.079 \text{ \AA}$, and $c = 13.890 \text{ \AA}$ for the SbF₆⁻ compound, $a = 13.975 \text{ \AA}$, $b = 12.954 \text{ \AA}$, and $c = 8.674 \text{ \AA}$ for the PF₆⁻ compound, and $a = 13.886 \text{ \AA}$, $b = 12.742 \text{ \AA}$, and $c = 8.178 \text{ \AA}$ for the BF₄⁻ compound.

For the PF₆⁻ and BF₄⁻ compounds the parameters a and b are comparable to the values of b and c found by Keller *et al* [11] for the Per(PF₆) samples. The c -values for our samples are approximately twice their a -values. However, when one small 2θ -value peak was omitted from our analysis the value of c dropped by half. This indicates that the previously quoted value may be unreasonably small due to peaks missing from the fit.

Table 2. A comparison of unit-cell parameters and cell volumes of (Per)₂BF₄, (Per)₂PF₆, and (Per)₂SbF₆ obtained by x-ray diffraction with similar reacted perylene compounds.

	a (Å)	b (Å)	c (Å)	Volume (Å ³)	
BF ₄	13.886	12.742	8.178	1447.0	
PF ₆	13.975	12.954	8.674	1570.3	
SbF ₆	21.079	21.079	13.890	6171.7	
AsF ₆	21.15	14.47	13.33	4079.5	[13]
PF ₆ (CH ₂ Cl ₂)	4.285	12.915	14.033	776.6	[11]
PF ₆ (THF)	4.26	12.79	13.89	756.80	[11]
AsF ₆ (CH ₂ Cl ₂)	4.294	13.077	14.132	793.55	[11]
Perylene	11.27	10.82	10.26	1250.9	[3, 4]
($\beta = 100.55^\circ$)					

The unit cell of the SbF₆⁻ compound has a similar $a:b:c$ ratio to the other compounds ($\sim 1.5:1.5:1$) but the lattice parameters are substantially larger. The a - and c -values

are similar to those for the $\text{Per}(\text{AsF}_6)_2$ compound [13] investigated by Datars *et al* ($a = 21.15 \text{ \AA}$, $b = 14.47 \text{ \AA}$, $c = 13.33 \text{ \AA}$) but the b -value is approximately 50% larger. These different lattice parameters follow the trend of increasing cell volume with increasing size of the reactant molecule. The cell volumes of the reacted compounds are larger than that of pure perylene for each of our compounds in contrast to the compounds of Keller *et al* as shown in table 2.

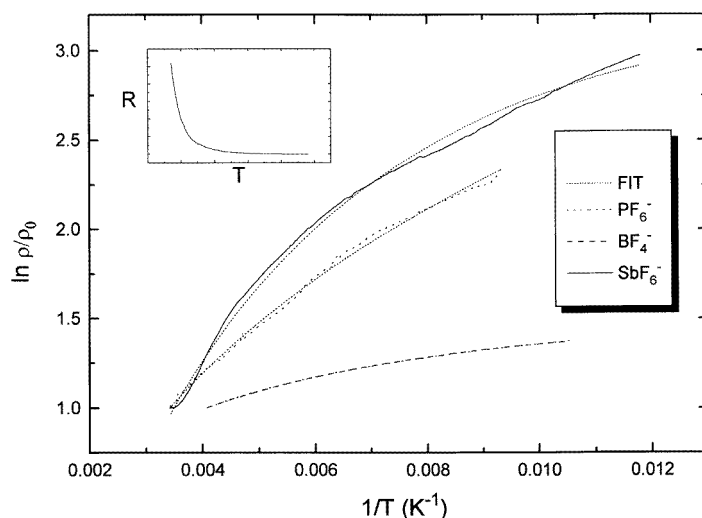


Figure 2. The natural log of resistivity divided by room temperature resistivity versus inverse temperature for $(\text{Per})_2\text{BF}_4$, $(\text{Per})_2\text{PF}_6$, and $(\text{Per})_2\text{SbF}_6$. Each curve has been independently fitted to the polaronic hopping resistivity described by equation (4). The inset shows resistance versus temperature for $(\text{Per})_2\text{SbF}_6$.

The pressed pellets of the reacted compounds had room temperature resistivities (ρ_0) prior to exposure to air of approximately $2\text{--}3 \text{ \Omega cm}$, 1.5 \Omega cm , and 700 \Omega cm for the SbF_6^- , PF_6^- , and BF_4^- compounds respectively. The temperature dependences of these samples all showed an increase in resistance with decreasing temperature. However, a plot of the natural log of the resistivity divided by the room temperature resistivity versus inverse temperature shows a downward curvature (see figure 2) contrary to a typical band-type semiconducting behaviour where the data should fit to a straight line.

Previous work on SbCl_5 -perylene complexes showed a similar decrease in the activation energy with decreasing temperature with the curvature attributed to a transition between two independent activation energies [10]. In our samples the plots of $\ln \rho/\rho_0$ versus $1/T$ show a much smoother curve which makes it difficult to define a distinct transition point from one activation energy to another. Furthermore, if a transition point is defined, the curves above and below this point still have a downward curvature and cannot be defined by the simple activation process.

Hall effect measurements were performed at room temperature on each of the reacted perylene compounds. However, in all cases the Hall voltage was too small to be detected at a field of 1.5 T. As a result, we can set an upper limit on the mobility of the carriers of $\mu \leq 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ if we exclude the remote case of exactly the same number of different charge carriers with the same mobility. This upper limit of the mobility is less than the lower limit of $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ set for delocalized-band-type conduction [14] indicating that

our systems have localized charge carriers that conduct through a hopping mechanism.

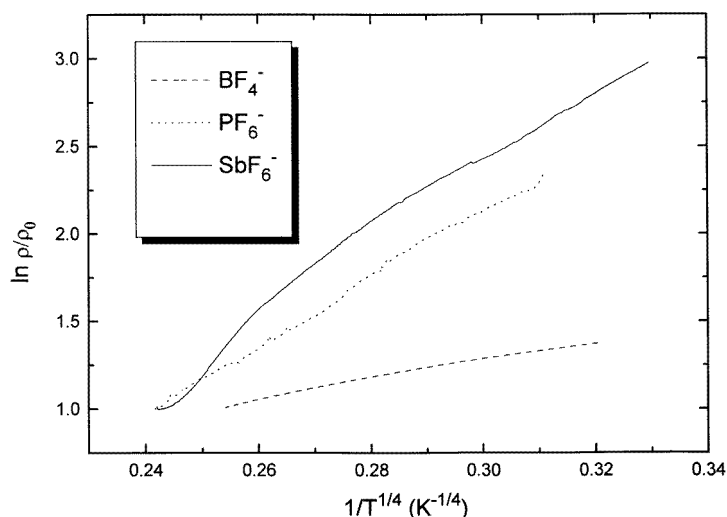


Figure 3. The natural log of resistivity divided by room temperature resistivity versus inverse temperature to the power 1/4 for $(\text{Per})_2\text{BF}_4$, $(\text{Per})_2\text{PF}_6$, and $(\text{Per})_2\text{SbF}_6$.

The proposal of hopping conduction rather than delocalized-band-type conduction provides an explanation of the curvature in the $\ln \rho/\rho_0$ versus $1/T$ plots. There are two scenarios that would provide for the necessary localized charge carriers that cause the hopping conduction in our materials. These are localization in a disordered system and localization in the small-polaron model. In the case of localization due to a disordered system the conduction can occur by nearest-neighbour or variable-range hopping. While nearest-neighbour hopping is an activated process, the activation energy should not have a strong temperature dependence. In the case of variable-range hopping, the conduction occurs so as to minimize the energy between hops and is not limited to hopping between nearest neighbours. This process gives a temperature dependence of the conductivity of

$$\sigma = \sigma_0 \exp(T_0/T)^{1/x} \quad (2)$$

where $x = 3$ or 4 for two-dimensional (2D) or three-dimensional (3D) conduction respectively [15]. When our data are plotted versus $1/T^{1/4}$ the data can be better fitted with a straight line than when they are plotted against $1/T$ (see figure 3). However, it is still not possible to get a perfectly straight fit and some curvature is still present in most results.

A small polaron occurs when a charge carrier is held at a fixed position in a solid. The presence of this excess charge produces a displacement in the position of the atoms in the vicinity of the excess charge and reduces the total energy of the system. The new positions of the surrounding atoms produce a potential well for the carrier, so it is 'self-trapped' and cannot move without an alteration of the positions of the neighbouring atoms. As a result, phonons are required to displace the atomic positions and allow for charge-carrier transport. In this case the hopping conductivity is given by

$$\sigma_h = \sigma_0 \exp(-E/kT) \quad (3)$$

with the activation energy E being a sum of the energy required to generate carriers and the activation energy associated with the intrinsic hopping of small polarons [16]. This

activation energy E can have some temperature dependence and this makes it possible to find a dependence that fits the curvature of our data.

If only single-phonon processes are considered with nearest-neighbour-activated hopping then the temperature dependence can be adequately described by equation (3). If, however, we consider multiphonon processes and intergrain effects in addition to the intragrain activation term then the conductivity can be described by

$$\sigma(T) = \sigma_1 \exp[-(T_0/T)^{1/4}] \exp(-T_1/T) \exp(-T_2/T) \quad (4)$$

as discussed by Zuppiroli and Forro [17]. The first term in this equation is a temperature-dependent jump rate for multiphonon processes where the polaronic situation is so localized that considering only single-phonon contributions is only appropriate at low (helium) temperatures. This term depends on temperature as $T^{1/4}$ over a large temperature range [16] as opposed to single-phonon processes which have a jump rate that is essentially independent of temperature. The second term in (4) is simply the contribution to the conductivity of the separation between hopping sites in space and energy and represents the conductivity network through each polycrystalline domain. This is equivalent to one-dimensional (1D) conduction from equation (2) which describes nearest-neighbour hopping. We assume our samples to have 3D conduction within the polycrystalline domains, but this single-exponential form is still valid because our x-ray diffraction data indicate that we do not have a disordered system and therefore can consider nearest-neighbour hopping. Finally, the third term in our expression is the contribution from the disorder in our samples that exists at length scales larger than the atomic or molecular scales described above. Since our study deals exclusively with pressed powder samples we have obviously introduced multiple intergrain boundaries that must be hopped over to connect the conducting domains. We would expect these boundaries to be isotropically distributed allowing us to introduce a single exponential with an activation energy of T_2 . If the intergrain resistances differ greatly then this form is still valid with the value of T_2 determined by a critical path method and depending on distribution of the energies. In summary the form of equation (4) contains contributions to the activation energy from the microstructure (T_2) and the energetic disorder (T_1) as well as a term describing the hopping frequency (T_0).

Using equation (4), we are able to fit all of our data (see figure 2). The values obtained for the disorder energies, $T_1 + T_2$, range from -992 to 548 K and the temperature T_0 varies between 2×10^3 and 1×10^9 K. These values are comparable with those obtained for other systems such as boron carbides, irradiated polymers, and disordered organic conductors [17].

In this analysis we have accounted for contributions to the conductivity that seem reasonable for our samples. The agreement between the experimental data and equation (4) indicates that the consideration of several contributing factors to the resistance is required. The assumption of polaronic hopping has been validated by the quality of the fits and makes use of the $\exp(1/T^{1/4})$ temperature dependence without the need to attribute this to variable-range hopping. There are numerous other possible contributions to the resistivity within the sample that we have not discussed because we have no concrete evidence of their existence. While other conduction mechanisms are possible, further discussion is not warranted by the information that is available for these systems.

4. Conclusions

Perylene was reacted with NO_2BF_4 , NO_2PF_6 , and NO_2SbF_6 to produce solvent-free $(Per)_2BF_4$, $(Per)_2PF_6$, and $(Per)_2SbF_6$. X-ray powder diffraction identified the unit cells of the compounds as being orthorhombic in the first two cases and tetragonal in the last case.

The lattice parameters obtained from fitting these data follow the trend of increasing cell volume with increasing size of the reactant molecule. The compounds had room temperature resistivities of 700 Ω cm, 1.5 Ω cm, and 2.5 Ω cm, respectively. The absence of solvent molecules in the resulting compounds allows us to attribute the conduction to charge transfer solely from the reactant molecules. All of the compounds exhibited an increase in resistance with decreasing temperature. However, a single activation energy typical of band-type semiconductors could not be obtained because of a downward curvature in the $\ln \rho/\rho_0$ versus $1/T$ curves. The conduction process has been attributed to polaronic hopping by fitting the data with a number of parameters accounting for multiphonon processes, intragrain and intergrain effects. This model fits the data well and accounts for the nonlinearity of the curves. Hall effect measurements placed an upper limit on the mobility of the carriers of $\mu \leq 0.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ supporting the claim of polaronic hopping being the dominant conduction mechanism in these samples.

Acknowledgments

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References

- [1] Sano M and Akamatsu H 1961 *Bull. Chem. Soc. Japan* **34** 1569.
- [2] Van Ewyk R L, Chadwick A V and Wright J D 1980 *J. Chem. Soc. Faraday Trans. I* **76** 2194
- [3] Camerman A and Trotter J 1964 *Proc. R. Soc. A* **279** 129
- [4] Donaldson D M, Robertson J M and White J G 1953 *Proc. R. Soc. A* **220** 311
- [5] Labes M M, Sehr R and Bose M 1960 *J. Chem. Phys.* **33** 868
- [6] Kommandeur J and Hall F R 1961 *J. Chem. Phys.* **34** 129
- [7] Kao H C I, Jones M and Labes M M 1979 *J. Chem. Soc. Chem. Commun.* **7** 329
- [8] Uchida T and Akamatsu H 1961 *Bull. Chem. Soc. Japan* **34** 1015
- [9] Akamatsu H, Inokuchi H and Matsunaga Y 1954 *Nature* **1973** 168
- [10] Blomgren G E and Kommandeur J 1961 *J. Chem. Phys.* **35** 1636
- [11] Keller H J, Nöthe D, Pritzkow H, Wehe D, Werner M, Koch P and Schweitzer D 1980 *Mol. Cryst. Liq.* **62** 181
- [12] Montgomery H C 1971 *J. Appl. Phys.* **42** 2971
- [13] Datars W R, Chien T R and Ummat P K 1995 *Can. J. Phys.* **73** 653
- [14] Bone S and Pethig R 1985 *J. Chem. Soc. Faraday Trans. I* **81** 537
- [15] Böttger H and Bryksin V V 1985 *Hopping Conduction in Solids* (Deerfield Beach, FL: VCH)
- [16] Emin D, Seager C H and Quinn R K 1972 *Phys. Rev. Lett.* **28** 813
- [17] Zuppiroli L and Forro L 1989 *Phys. Lett.* **141A** 181