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BUDAPEST

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ABSTRACT

Conductivity and paramagnetic susceptibility of N-alkyl-isoquinolinium--TCNQ complexes were measured. In the case of isopropyl derivative the simultaneous appearance of two compounds was found: one of metallic (1:2 composition) character, the other of semiconducting (2:3) thermally activated char-

АННОТАЦИЯ

Мы измеряли электропроводность и парамагнитную восприимчивость N-алкил--изоквинолиниум-ТЦНХ комплексов. В случае изопропиловых производных мы наблюдали одновременное образование металлического (1:2)состава и термически активируемого полупроводникового (2:3) комрлексов.

KIVONAT

N-alkyl-isoquinolinium-TCNQ complexek vezetőképességét és paramágneses szuszceptibilitását vizsgáltuk. Az isopropyl lánccal szubsztituált donor molekula esetén egyedidejüleg egy fémes viselkedésü (1:2 összetételü) és egy termikusan aktiválható félvezető (2:3) komplex jött létre.

In recent years a large number of highly conducting CT complexes have been found. Because their physical and chemical properties leading to high conductivity are not fully understood, in a previous paper we investigated the effect of donor on a series of N-alkyl-quinolinium $(TCNQ)_2$ complex salts [1]. In this series the methyl and ethyl derivatives show a distinct solvent effect [2,3] if the chain length is increased an alternating structure is built up [4] and as a consequence the paramagnetic susceptibility and conductivity show an activated character [5]. The activation energy of ESR intensity progressively grows with the chain length in the N-propyl-isopropyl-N-butyl Q-series.

Here the ESR susceptibility and d.c. conductivity of TCNQ complexes with the N-alkyl derivatives of the isoquinolinium (IQ) donor are discussed.

The alkyl derivatives were prepared by the well-known method, quaternizing the IQ donor with the appropriate alkyl-J. The complexes were obtained by the diffusion method.

The IQ-series shows different features from the complexes of N-alkyl-Q donors: the composition of the complexes are not always 1:2, the propyl complex has a stoichiometry of 2:3, whereas the isopropyl one crystallizes in two distinct forms with different composition (see Table I). The crystal structure has not been determined for these complexes.

The temperature dependence of the paramagnetic susceptibility was measured by integrating the area under the ESR spectra taken at X-band by a JEOL spectrometer. The ESR intensities are normalized to the static room temperature susceptibility (corrected for diamagnetic contribution) of the $Q(TCNQ)_2$ reference powder sample. The d.c. conductivity was measured by the four probe method.

Only the methyl-IQ product is analogous with the me-Q complex: the susceptibility does not change with temperature (Fig. 1a), the ESR linewidth has a relatively low and constant value (Fig. 2a). The d.c. conductivity at room temperature has a slightly higher value than $Q(TCNQ)_2$ and shows metallic behaviour (Fig. 3a).

The n-propyl-IQ 2:3 complex has a reduced susceptibility slowly decreasing with temperature (Fig. 1b), the narrow linewidth changes in the same manner (Fig. 2b). Its conductivity is relatively high (50-100 $\Omega^{-1}cm^{-1}$ at room temperature), showing a definitely activated character (Fig. 3b).

In the case of the N-butyl IQ complex the composition is not well defined, the susceptibility is nearly constant till 200 K, below this temperature a small activation can be detected and the linewidth is slightly increasing (Figs 1,2c). This is in accordance with conductivity measurements where the slope changes at this temperature giving a relatively large gap (0.25 eV) at lower temperatures (Fig. 3c).

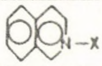
Characteristic polymorphism was found by the isopropyl-IQ complex: the needle-like crystal form A, with stoichiometry 1:2, shows high conductivity (10 $\Omega^{-1}cm^{-1}$) and metallic behaviour (Fig. 3d), in accordance with the temperature independent susceptibility (Figs 1,2d).

Whereas the small platelets of form B, with a stoichiometry 2:3, are semiconducting: $\sigma_{RT} = 5 \cdot 10^{-3}\ \Omega^{-1}cm^{-1}$, with a gap of $E_{\sigma} = 0.27$ eV (Fig. 4). ESR intensity shows an activation energy $E_a = 0.1$ eV above room temperature, with a linewidth change characteristic of the fast exchange region (Fig. 2e). Fine structure was not detectable at lower temperatures because of the samll size of the single crystal samples.

Summarizing the experimental results (Table I) the most striking feature is the high room temperature conductivity -10 to 100 $\Omega^{-1}cm^{-1}$ (except e) - of the complexes with these sizable asymmetrical donors.

The metallic behaviour in the case of the methyl and the isopropyl A-complex can be ascribed to a disorder, which is believed to play a role in preventing the development of a semiconducting structure.

Table I. Electric and magnetic properties of N-alkyl-IQ-TCNQ complexes

	Composition	χ_T, E_a eV	σ_T, E eV
a. methyl	1:2	const.	metallic
b. propyl	2:3	const.	0.08
c. butyl	1:1.8	0.05	0.25 $<$200 K
d. isopropyl A	1:2	const.	metallic
e. isopropyl B	2:3	0.1	0.27

Samplex of n-propyl and n-butyl complexes showing activated character need further investigation for solvent effect and susceptibility measurements at lower temperatures.

The simultaneous appearance of metallic and semiconducting species - from isopropyl A and B complexes - has also been evidenced by aminopyridine complexes [6]. Radical salts with metallic behaviour were synthesized in a number of cases by a rapid cooling of the reaction mixture after mixing together the reagents. If heating was continued only nonconducting materials were produced. The authors suggested that complexes with metallic behaviour tend to be kinetic products and can be transformed into semiconducting thermodynamic compounds by heating in a solvent. This supposition may hold also for our isopropyl complex, prepared by a slow diffusion method.

FIGURE CAPTIONS

Fig. 1. Relative susceptibility as a function of temperature, normalized to the static susceptibility of $Q(TCNQ)_2$ complex salts

Fig. 2. ESR linewidth as a function of temperature

Fig. 3. log of normalized d.c. conductivity as a function of $10^3/kT$

Fig. 4. Activation energy of susceptibility and conductivity of $(N\text{-isopropyl-isoquinolinium})_2(TCNQ)_3$ complex salt

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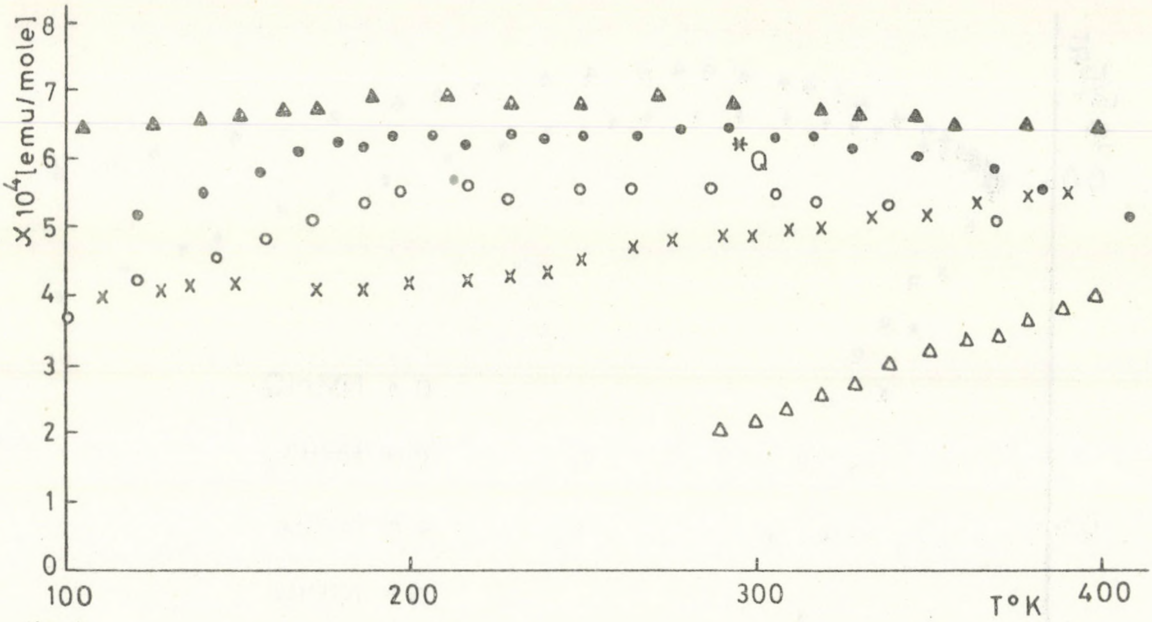
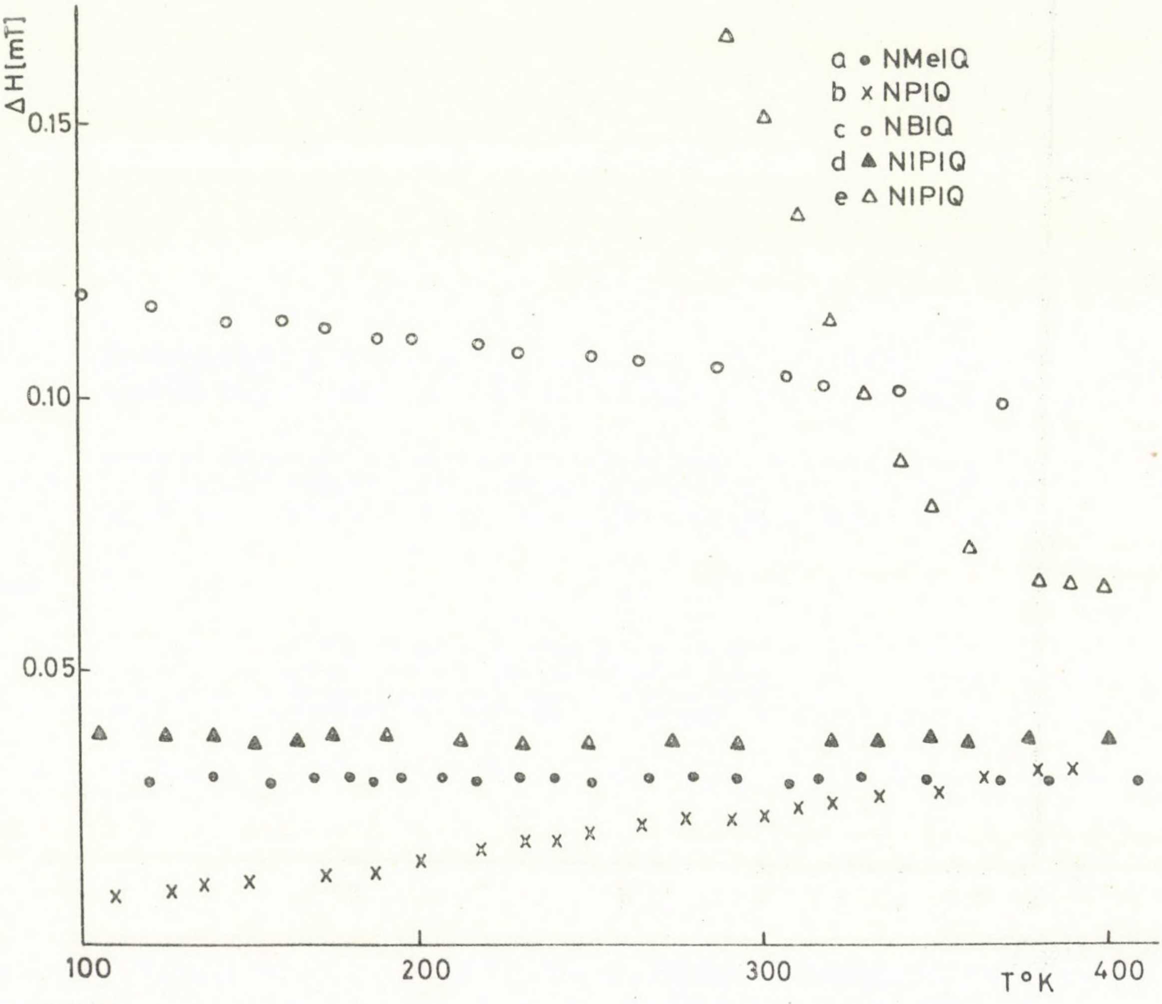


χ 10⁴ [emu/mole]
0
1
2
3
4
5
6
7
8
100
200
300
400
T°K
Q

fig.1.



ΔH [mT]
0.05
0.10
0.15
a • NMeIQ
b x NPIQ
c o NBIQ
d ▲ NIPIQ
e △ NIPIQ
100
200
300
400
T°K

fig. 2.

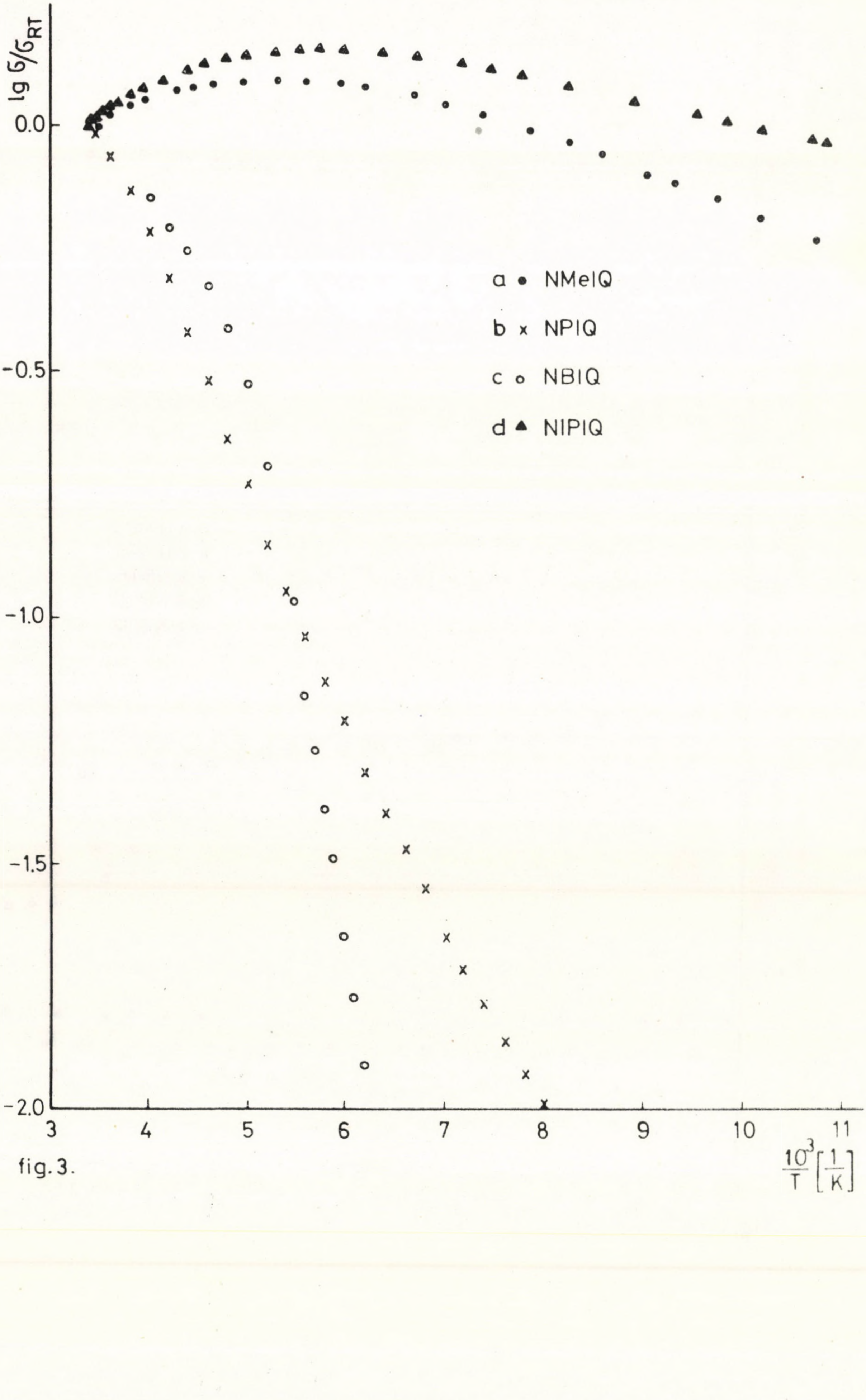
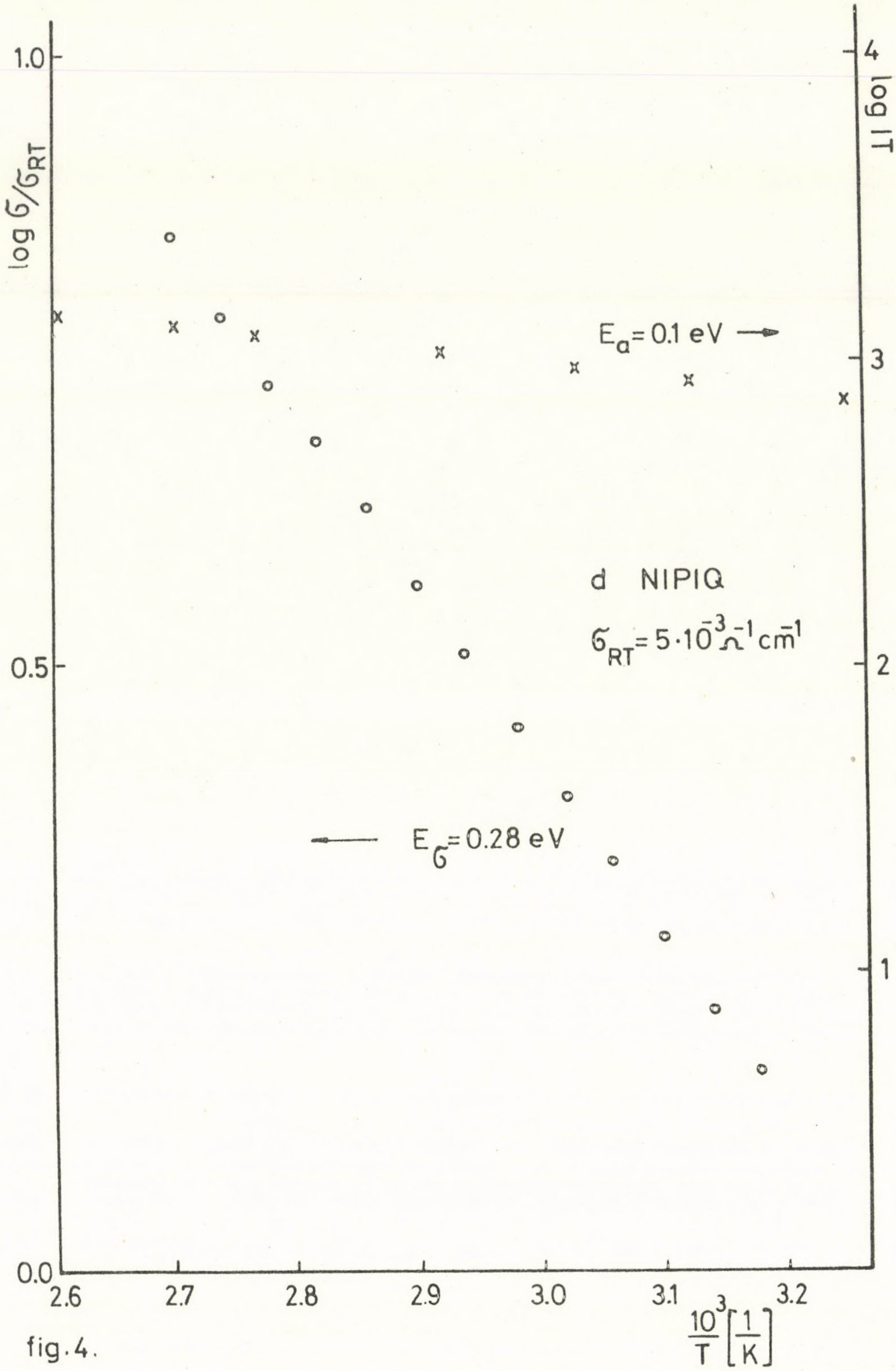

lg σ/σ_RT
0.0
-0.5
-1.0
-1.5
-2.0
3
4
5
6
7
8
9
10
11
a • NMeIQ
b x NPIQ
c o NBIQ
d ▲ NIPIQ
10^3/T [1/K]

fig. 3.



log σ/σ_RT
log IT
1.0
0.5
0.0
4
3
2
1
E_a = 0.1 eV
d NIPIQ
σ_RT = 5·10^-3 Ω^-1 cm^-1
E_σ = 0.28 eV
2.6
2.7
2.8
2.9
3.0
3.1
3.2
10^3/T [1/K]

fig.4.

Kiadja a Központi Fizikai Kutató Intézet
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Felelős vezető: Nagy Károly
Budapest, 1981. augusztus hó