SPECTROSCOPIC INVESTIGATIONS OF CHARGE TRANSFER SALT VINΦ$_2$(TCNQ)$_2$

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VINΦ$_2$(TCNQ)$_2$ is a salt with two different, non-parallel TCNQ stacks. The polarized reflectance spectra from single crystals in the IR region 660–5200 cm^{-1}, the powder absorption spectra 400–45000 cm^{-1} and FT–NIR Raman spectra of VINΦ$_2$(TCNQ)$_2$ are measured at room temperature. Moreover, the temperature dependence of powder absorption spectra in the frequency range 400–7900 cm^{-1} are studied. The nature of electronic bands, the anisotropy of optical conductivity, the temperature dependence of some vibrational bands and the charge distribution on different TCNQ stacks are discussed.

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1. Introduction

In conducting charge transfer salts based on tetracyanoquinodimethane (TCNQ) and various electron donors the TCNQ molecules stack face-to-face to form linear chains with significant overlap of π-molecular orbitals and high density of radical electrons. In most salts the TCNQ chains are equivalent and parallel each to other but also crystals with two different, non-parallel TCNQ stacks are known [1, 2]. Such extraordinary crystal structure has been also discovered in the salt VINΦ$_2$(TCNQ)$_2$, where VINΦ$_2$ is vinamidinium [3]. The aim of this paper is to study the electronic and vibrational spectra of VINΦ$_2$(TCNQ)$_2$ crystals; some preliminary data were published in Ref. [4].

In VINΦ$_2$(TCNQ)$_2$ the TCNQ molecules stack in two columns which differ in the orientation of their axes: one column is parallel to the a-axis of the unit cell (TCNQ A) and the second one is parallel to the b-axis (TCNQ B) forming an angle close to 120°. The TCNQ A and TCNQ B stacks are arranged to form separate layers parallel to (001) crystal face alternating with cationic layers. From the TCNQ bond lengths results that molecules in both stacks have different ionicity with the values nearly $(2/3)e^-$ for TCNQ A and $(1/3)e^-$ for TCNQ B. The TCNQ A molecules are linked to VINΦ$_2$ cations by hydrogen bonds [3].

The existence of two different TCNQ stacks and the inequivalency of charge distribution is rationalized in terms of hydrogen bonding. Such strong interaction of TCNQ A chains with cations should cause a pinning of electrons. As results from magnetic and electrical properties, the higher charged TCNQ A stack is semiconducting, whereas the lower charged TCNQ B stack is probably metallic [3]. The different electrical properties of both stacks should have an influence on electronic spectra of $VIN\Phi_2(TCNQ)_2$ in the charge transfer (CT) band region.

Usually for TCNQ salts, when the electrical vector of polarized IR radiation is parallel to TCNQ stack, the spectrum consists of a strong charge transfer band and a series of strong oscillation features related to the coupling of electrons with the totally symmetric intramolecular TCNQ vibrations (a_g modes), whereas for perpendicular polarization the IR spectrum is weak and nearly frequency independent [5]. In $VIN\Phi_2(TCNQ)_2$ such anisotropy is not observed since for each polarization both stacks contribute to IR spectrum. Moreover, as the stacks exhibit different electrical properties, their IR spectra should be also different.

2. Experimental

The procedure of $VIN\Phi_2(TCNQ)_2$ crystal preparation was described in Ref. [3]. We studied the absorption spectra of powdered $VIN\Phi_2(TCNQ)_2$ crystals dispersed in KBr pellets in the frequency range 400–45000 cm^{-1} at room temperature. For comparison the analogical measurements of the salts $VIN\Phi_2BF_4$ and $VIN\Phi_2I$ were also performed. Three different spectrometers were used: FT–IR Perkin Elmer 1725 X (400–7900 cm^{-1}), Specord NIR (4000–13500 cm^{-1}) and Specord UV–VIS (13000–45000 cm^{-1}). Moreover, we measured the temperature dependence of powder absorption spectra of $VIN\Phi_2(TCNQ)_2$ in the frequency range 400 cm^{-1} to 7900 cm^{-1}. The reflectance spectra in polarized light taken from $VIN\Phi_2(TCNQ)_2$ single crystals were recorded over the spectral range 660–5200 cm^{-1} by using the FT–IR Perkin Elmer 1725 X spectrometer equipped with a FT–IR microscope. The reflectance spectra were measured from the best developed crystal face (001), parallel to the conducting TCNQ layers, for various orientations of the electrical vector of polarized light (angular dependence). The Kramers–Kronig analysis of reflectance spectra was carried out to obtain the optical conductivity spectra. Outside the measured frequency region, the reflectance spectra were extrapolated by taking into account the data for other TCNQ complex salts [6, 7]. The FT–NIR Raman spectra were obtained for $VIN\Phi_2(TCNQ)_2$ as well as $VIN\Phi_2BF_4$ and $VIN\Phi_2I$ powders by using FT-IR Bruker IFS 66 spectrometer with Raman FRA 106 accessory and Nd:YAG laser ($\lambda = 1.064$ μm).

3. Results and discussion

3.1. Electronic spectra

The electronic spectrum of $VIN\Phi_2(TCNQ)_2$ powders (Fig. 1) consists of four strong bands centered at about 4000, 12000, 16500, 27000 cm^{-1} and is similar to the spectra of other complex TCNQ salts. The band centered at 12000 cm^{-1} is a superposition of three components at about 10000, 11500 and 13000 cm^{-1}. The band of 4000 cm^{-1} is related to the charge transfer: ($TCNQ^- + TCNQ^0 \rightarrow$

TCNQ^0+TCNQ$^-$) and in powder spectrum it is a superposition of CT excitations in A and B stacks. The analogous CT band in the reflectance spectra of a single crystal (Fig. 2. and Fig. 3) is shifted towards lower frequencies (maximum at about 3400 cm^{-1}). This frequency difference can be explained by an influence of grinding and/or compacting of the sample (some differences are also observed for vibrational bands). It is known that grinding of TCNQ salts can shift the charge transfer band to higher frequencies [8].
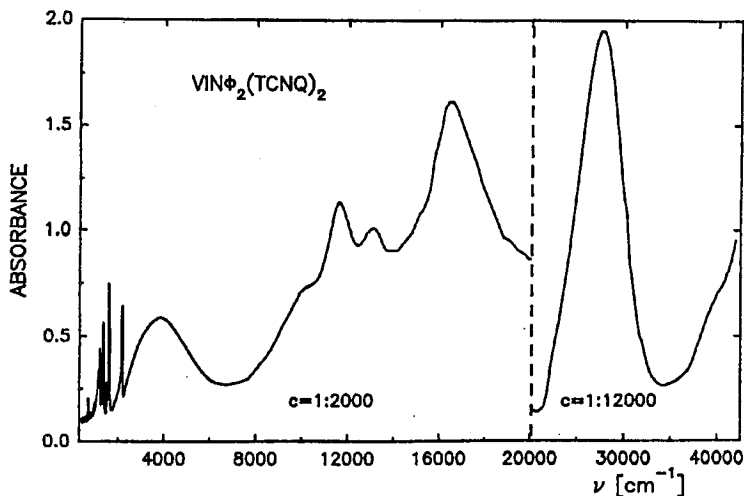

Fig. 1. Electronic absorption spectra at room temperature of VINΦ_2(TCNQ)$_2$ powders in KBr pellets (weight concentration 1:2000 and 1:12000).

In general, the CT band in TCNQ salt exhibiting metallic properties is broader and its maximum lies at lower frequency in comparison to the analogous band in semiconducting salt. The analysis of the reflectance spectra of VINΦ_2(TCNQ)$_2$ crystal for different polarizations shows that the CT band of stack A has higher intensity than the one of stack B (as should be expected) and the bands of both stacks are situated at similar frequencies. Such CT band similarity suggests that both stacks exhibit semiconducting properties.

In comparison to other electronic bands the band at 27000 cm^{-1} in the spectra of VINΦ_2(TCNQ)$_2$ powders exhibit an anomalously strong intensity (Fig. 1). The investigations of electronic spectra of VINΦ_2BF$_4$ and VINΦ_2I revealed the existence of strong absorption at the same frequency, therefore, the band 27000 cm^{-1} in VINΦ_2(TCNQ)$_2$ should be considered as a superposition of intramolecular electronic excitations of both TCNQ and VINΦ_2 molecules.

3.2. Vibrational spectra

The IR reflectance spectra of VINΦ_2(TCNQ)$_2$ crystals are dominated by VINΦ_2 bands and bands resulting from vibronic activation of TCNQ (Fig. 2 and Fig. 3). The bands at about 1630, 1580, 1489, 1336, 1301, 1191, 1157, 847, 763 cm^{-1}
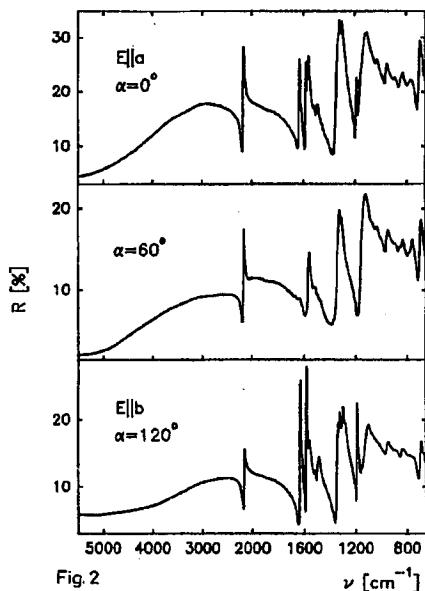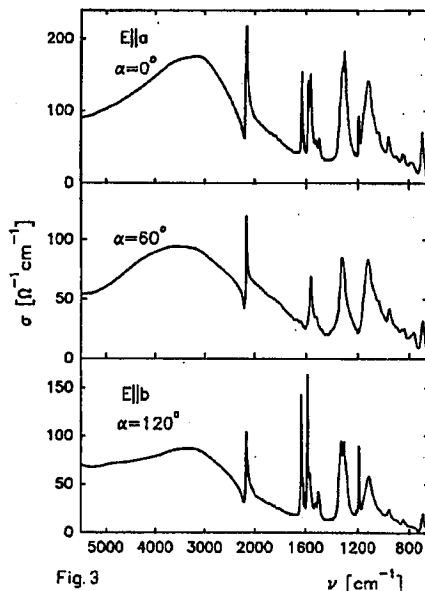
Fig. 2. Polarized infrared reflectance spectra from (001) crystal face of VINΦ₂(TCNQ)₂ at room temperature for electrical vector of IR light parallel to: a-axis ($E \parallel a$, $\alpha = 0°$), direction of minimum intensity of VINΦ₂ bands ($\alpha = 60°$) and b-axis ($E \parallel b$, $\alpha = 120°$). Note the different reflectance scales.

Fig. 3. Infrared conductivity spectra of VINΦ₂(TCNQ)₂ derived from reflectance spectra by Kramers–Kronig transformation for different polarizations (compare Fig. 2). Note the different conductivity scales.

are related to the VINΦ₂ cation (analogous bands were found in IR spectra of VINΦ₂BF₄ and VINΦ₂I salts). The bands assigned to activated a_g modes of TCNQ lie at nearly the same positions as in the spectra of other complex TCNQ salts [5], i.e. at 2160, 1561, 1320, 1120, 951, 689, 608 cm⁻¹ for ν = 2, 3, 4, 5, 6, 7, 8 a_g modes, respectively. The two-column stacking leads to an unusual anisotropy of the polarized reflectance spectra. The angular dependence of different TCNQ bands is similar, i.e. the intensity extrema are situated at the same positions (Fig. 4). The reflectance spectrum is dominated by a contribution from TCNQ A chain, therefore, the maximum intensity of TCNQ bands coincides with the a direction and the minimum of intensity is shifted by 90°. The intensity extrema of VINΦ₂ bands are shifted by about 30° with respect to TCNQ bands (Fig. 4). Taking into account that for the electrical vector of polarized light perpendicular to TCNQ chains the reflection coefficient is nearly constant, one can assume that for polarization perpendicular to TCNQ A stacks ($E \perp a$) the IR spectrum is mainly generated by TCNQ B stack. Surprisingly, considering TCNQ bands, the spectrum for polarization $E \perp a$ is qualitatively similar to that observed for polarization $E \parallel a$, nevertheless the intensities are different. This fact suggests again that both stacks exhibit semiconducting behavior. The TCNQ molecules in both stacks are ar-
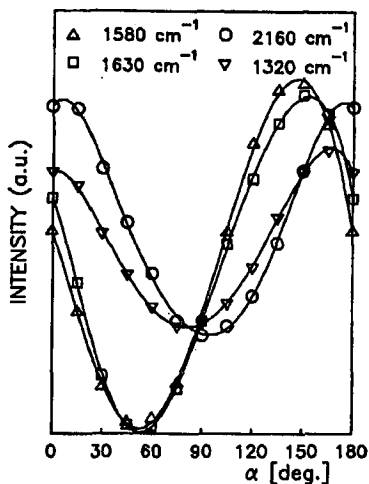
Fig. 4. Intensities of selected IR bands in $VIN\Phi_2(TCNQ)_2$ reflectance spectrum for different polarizations of incident light (angular dependence). The TCNQ bands: 2160 and 1320 cm^{-1}; the $VIN\Phi_2$ bands: 1630 and 1580 cm^{-1}.

ranged in diads [3], therefore, if the assumption about semiconducting behavior is true, the best approach for description of the electron–molecular vibration coupling phenomena would be the model of weakly interacting dimers [9], but with different charge densities: $(2/3)e^-$ for TCNQ A and $(1/3)e^-$ for TCNQ B molecules. In this way the IR spectrum of $VIN\Phi_2(TCNQ)_2$ would be a superposition of the spectra of non-parallel, dimerized TCNQ chains with different charge densities. The IR bands, which are the consequence of electron–intramolecular vibration coupling, exhibit strong temperature dependence, whereas the changes of the normal IR active vibrations are usually weaker [5]. From our investigations it results that not only the TCNQ bands of a_g symmetry but also some bands of $VIN\Phi_2$ cation are strongly susceptible to temperature variation. In Fig. 5 we show the T-dependence of two $VIN\Phi_2$ bands at 1628 cm^{-1} and 1580 cm^{-1} (C=C and C=N vibrations of the diazapentadiene bridge) in comparison with a_g bands of TCNQ (2180 cm^{-1} and 1324 cm^{-1}). It seems that enhancement of some intramolecular vibrations of $VIN\Phi_2$ cation can be explained by a coupling of intramolecular charge transfer with C=C and C=N vibrations in the diazapentadiene bridge. This approach is analogous to that described by Yartsev and Jacobsen [10] who considered the coupling of intramolecular CT with antisymmetric modes of TCNQ.

In the FT–NIR Raman spectrum of $VIN\Phi_2(TCNQ)_2$ powders (Fig. 6) we find the bands at 2206, 1599, 1424, 1197, 960, 715, 608, 331, 156 cm^{-1} which are related to $\nu = 2, 3, 4, 5, 6, 7, 8, 9, 10$ TCNQ a_g modes, respectively. The absence of $VIN\Phi_2$ bands can be interpreted in terms of a strong absorption of NIR radiation by conducting $VIN\Phi_2(TCNQ)_2$ crystal. The a_g modes of TCNQ are probably excited by resonance Raman mechanism, therefore, they are strong enough to be observed in the spectrum. The position of Raman bands is dependent on averaged
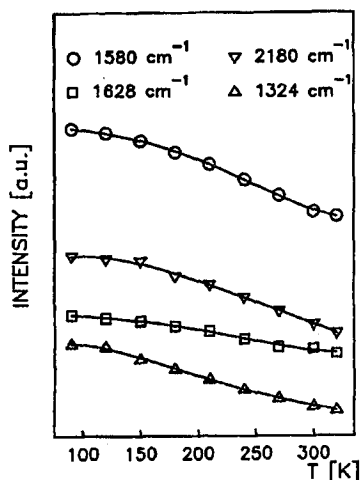
Fig. 5. Temperature dependence of selected IR bands in absorption spectra of VINΦ$_2$(TCNQ)$_2$ powders in KBr pellets (peak intensities). TCNQ bands: 2180 cm^{-1} and 1324 cm^{-1}; VINΦ$_2$ bands: 1580 cm^{-1} and 1628 cm^{-1}.
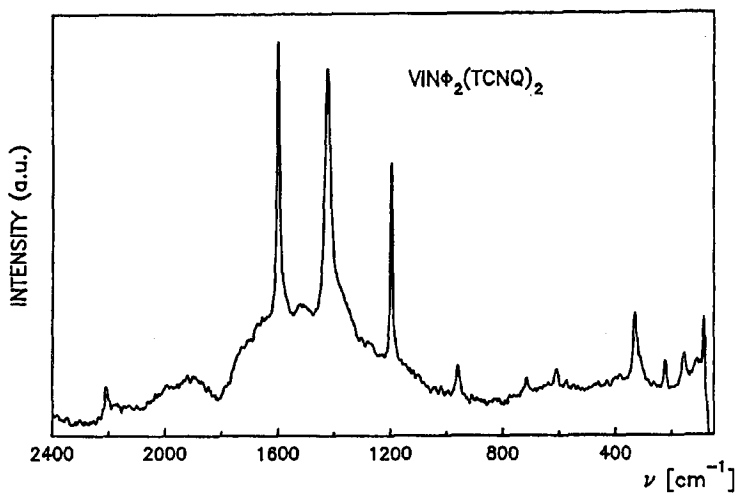

Fig. 6. FT–NIR Raman spectrum of VINΦ$_2$(TCNQ)$_2$ powder at room temperature (excitation $\lambda = 1.064\ \mu$m).

charge density on TCNQ molecule. The most sensitive to charge density changes is the mode $\nu_4(a_g)$ [11] which appears in the spectrum of VINΦ$_2$(TCNQ)$_2$ as a single line at 1424 cm^{-1} (not a doublet) and suggests that the TCNQ ionicity in both stacks is the same and equals about $(1/2)e^-$; similar conclusion results from the analysis of the other TCNQ a_g bands. This is in disagreement with the

values estimated from bond lengths analysis [3] by the method of Flandrois and Chasseau [12]. The disagreement can be related to the fact that the Raman spectra were studied in powdered samples and the properties of powder are often different from those of bulk crystals. On the other hand, the method of estimation of charge density on the basis of bond lengths is approximative and in the case of such strong donor–acceptor interactions as in $VIN\Phi_2(TCNQ)_2$ (hydrogen bonding) can yield relatively large errors. In our opinion, however, in this stage of investigations the explanation of Raman data in terms of the influence of powdering seems to be a better one, since the IR reflectance spectra from single crystals show the considerable anisotropy of intensity supporting thus the different ionicity of TCNQ molecules in both stacks.

In conclusion, on basis of our spectroscopic studies of $VIN\Phi_2(TCNQ)_2$ salt we suggest that both stacks exhibit semiconducting behavior.

Acknowledgments

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