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LA-UR--88-2265

DE88 014325

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SUBMITTED TO: Proceedings of ICSM 1988 Conference, June 26-July 2, Journal
of Synthetic Metals.

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THE INTRINSIC ENERGY GAP OF CRYSTALLINE TRANS-POLYACETYLENE

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ABSTRACT

Experimental data for the anisotropic optical conductivity of highly oriented non-fibrous trans-polyacetylene films and first-principles electronic structure calculations of crystalline 3-D trans-polyacetylene are presented. A comparison between the experimental data and the calculated density of states reveals that three-dimensional crystalline *trans*-polyacetylene has a direct minimum energy gap of 1.1 eV.

INTRODUCTION

The optical band gap absorption in *trans*-polyacetylene clearly exhibits the quasi-one-dimensional character of *trans*-(CH)_x [1-6]. However, the singularity at the band edge, which is predicted to occur in strictly one-dimensional (1-D) systems, is substantially broadened. The data show an extended tail in the region near the onset of absorption. Whereas the steep portion in the absorption spectrum can be assigned to a direct "one-dimensional" (1-D) gap, the interpretation of the absorption tail and, consequently, the determination of the intrinsic minimum gap of crystalline *trans*-(CH)_x is less straightforward. The absorption tail reflects partially the disordered character of the samples and partially the intrinsic three-dimensional character of the crystals. Fincher *et al.* [1] concluded from optical measurements in Shirakawa material that *trans*-(CH)_x has a 1-D gap E^{1D}_{gap} of 1.4 eV and an indirect "three-dimensional" minimum gap E_{gap} of about 1.1 eV. Optical data of *trans*-(CH)_x under pressure [2] yielded somewhat higher values, namely $E^{1D}_{gap}=1.7-1.8$ eV and the minimum gap $E_{gap}=1.45 \pm 0.05$ eV. Most recent measurements indicate a band gap of crystalline *trans*-(CH)_x close to 1.5 eV [3-6].

Still, a precise experimental determination of the actual intrinsic minimum gap of *trans*-(CH)_x is hampered by the inadvertent defects and broken chains in the material

which make it difficult to assign the observed broadening and the band edge tail in the absorption spectrum unambiguously either to 3-D interchain coupling effects or to defects.

In this paper we present optical absorption data on highly oriented non-fibrous trans-polyacetylene films and first-principles electronic structure calculations of crystalline 3-D trans-polyacetylene. We show that a comparison between the predicted joint density of states and the measured optical absorption coefficient allows an accurate determination of the intrinsic minimum energy gap of *trans*-polyacetylene.

EXPERIMENT

Highly oriented non-fibrous trans-polyacetylene films have been prepared by a precursor polymer route which is described in detail in [7]. The material has a density of 1.15 g/cm³ which is close to the crystallographic value. The stretching ratios lie between 15 and 20 for the samples investigated. Accordingly, the misalignment of the polymer chains is smaller than 5 degrees, as follows from the width of the relevant X-ray diffraction peaks. All experiments have been performed exclusively in high vacuum or in high-purity argon atmosphere. Polarized optical reflectivity measurements have been carried out in a wide frequency range between 0.025 eV and 4.1 eV at nearly normal incidence. The anisotropic optical constants and the dielectric function for *trans*-(CH)_x have been derived from a Kramers-Kronig analysis which takes into account multiple reflection and interference effects in a self-consistent way [8]. The high quality of the surface in our samples strongly reduces the diffuse scattering – which is present in material with fibrous morphology (Shirakawa-type material) [1] – and allows a quantitative analysis of the optical absorption in the band tail regime.

Fig.1. Optical conductivity of *trans*-polyacetylene. Dotted line: parallel optical conductivity determined from data in stretch-oriented Shirakawa polyacetylene [1].

Figure 1 shows the spectral dependence of the optical conductivity $\sigma(\omega) = \omega \epsilon_2(\omega)/4\pi$, with ϵ_2 denoting the imaginary part of the dielectric function. The conductivity $\sigma_{//}$ parallel to the chain axis shows a narrow peak located at 1.74 eV with a value of nearly $7000 \Omega^{-1} \text{ cm}^{-1}$ at the maximum. The spectrum of $\sigma_{//}$ obtained from reflectivity measurements on stretch-oriented Shirakawa-type polyacetylene [1] (ST) is also shown in Fig. 1. The energetic position of the peaks in the two materials coincide, but the maximum value of the conductivity in our material is nearly twice that of ST. The coincidence of the maxima indicates that the conjugation lengths in our material are comparable to that in ST-polyacetylene. The high degree of orientation and the reduced diffuse scattering in our compact samples with non-fibrous morphology increases the parallel reflectivity in the absorptive region and decreases it in the region below the band edge. As a consequence, we conclude that the tail in the ST material is caused by diffuse scattering and is not due to intrinsic absorption.

The energetic positions of the maxima of $\alpha_{//}$ (1.9 eV) and $\sigma_{//}$ (1.8 eV) were previously obtained in [9] from electron-energy loss-spectroscopy (EELS) measurements and by extrapolating the EELS data to zero momentum transfer. The present optical data are in excellent agreement with these results.

In Fig. 3 (thin line) we present the spectral dependence of the absorption coefficient $\alpha_{//}$ for parallel polarization. The maximum appears at 1.9 eV, with a value of $\alpha_{//} = 7.4 \cdot 10^5 \text{ cm}^{-1}$. This value is fully consistent with data from EELS [10], even though the latter measurements were carried out on very thin samples (around 2000 Å), whereas the present experiments have been performed on samples with a few microns thickness. In addition to the peak position, the anisotropy of the absorption has also been measured. We find the anisotropy, $\alpha_{\perp}/\alpha_{//} = 26$ at the peak position, again in excellent agreement with the EELS data [10].

THEORY

We now show that a comparison of these optical band edge absorption data in *trans*-polyacetylene with first-principles calculations of the joint density of states provides an accurate value for the minimum band gap of *trans*-(CH)_x.

The transition rate for optical absorption – sufficiently close to the band edge – is proportional to the joint density of states. In a one-dimensional system, the joint density of states is singular at the band edges and varies as $(E-E_{\text{gap}})^{-1/2}$ for energies E close to the band edge [1]. In three-dimensional systems, on the other hand, the joint density of states varies as $(E-E_{\text{gap}})^{1/2}$ for optically allowed direct transitions and as $(E \pm \hbar\omega_{\text{ph}} - E_{\text{gap}})^2$ for indirect transitions. The latter require a phonon with energy $\hbar\omega_{\text{ph}}$ to participate in the transition.

We have performed extensive electronic structure calculations of crystalline 3-D *trans*-(CH)_x, employing parameter-free local-density-functional theory (LDA) [11] with *ab-initio* norm-conserving pseudopotentials for carbon [12] in a momentum-space

Fig. 2. Calculated electronic density of states (normalized to 2 electrons per band) in 3-D crystalline *trans*-(CH)_x in the P2₁/a structure.

Fig. 3. Experimental absorption coefficient of *trans*-polyacetylene (thin line) and calculated joint density of states (thick line). The maximum value of the absorption coefficient has been adjusted to the maximum in the joint density of states in this figure.

representation [13]. The exchange-correlation energy has been evaluated with the functional given by Painter [14]. The Kohn-Sham equations [13] have been solved in a 1400 plane-waves basis (corresponding to a maximum kinetic energy of 30 Rydbergs).

The experimental structural data indicate that *trans*-(CH)_x has a monoclinic unit cell with two possible configurations having been proposed, either an in-phase (P2₁/a) [15] or an anti-phase arrangement (P2₁/n) [16] of the dimerized backbone. As discussed in detail in [17], our first-principles calculations show that the P2₁/a structure is lower in total energy and therefore favored in perfectly ordered, pure crystalline material.

In Fig. 2 we show the calculated density of states of *trans*-(CH)_x in the P2₁/a structure. There is an approximately symmetric splitting of the topmost valence and lowest conduction bands which leads to a broadening of the 1-D singularity in the density of states. The electronic band structure reveals that the band edge is direct with an onset in the density of states which is characteristic in 3-D systems.

The joint density of states close to the band edge is depicted in Fig.3 (thick line) and compared with our optical absorption data.

A direct comparison between the local density functional calculations and the experimental data is not possible since this method does not give the optical gap. However, the excited quasi-particle eigenvalues in an insulator or semiconductor have been shown to differ from the local density band structure to an excellent level of approximation by a wave-vector independent self energy Σ_{el} which rigidly shifts the conduction bands upwards [18]. Rather than attempting to determine this shift from first-principles, we have sidestepped this calculation and fitted the steep "one-dimensional" gap E^{1D}_{gap} portion in the calculated joint density of states to the experimental data.

If we take a value of $\Sigma_{el} = 0.74$ eV, theory and experiment are in excellent agreement as shown in Fig. 3. This procedure therefore allows an accurate determination of the intrinsic minimal energy gap of crystalline 3-D *trans*-polyacetylene; from Fig. 3 we can deduce its value to be 1.1 eV. The experimental band edge data show a tail which is more extended than that of the calculated joint density of states, clearly showing the effect of defects and imperfections which are not intrinsic to perfect crystalline material. One may also deduce a "one-dimensional" gap of 1.4 eV from the results depicted in Fig. 3.

In conclusion, we find that three-dimensional crystalline *trans*-polyacetylene has a direct minimum energy gap of 1.1 eV.

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