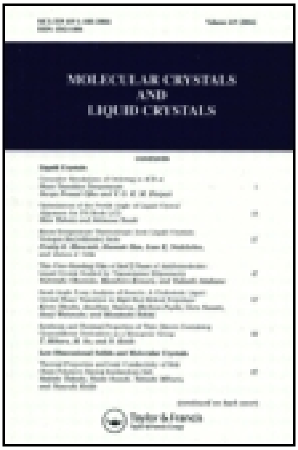

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Infrared Absorption in Quinolinium Di-Tetracyanoquinodimethanide

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INFRARED ABSORPTION IN QUINOLINIUM DI-TETRACYANOQUINODIMETHANIDE

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Abstract The absorption by Qn(TCNQ)$_2$ has been studied between 50 and 4000 cm^{-1} at temperatures from 4 K to 300 K. Infrared activity of the a$_g$ phonon modes of TCNQ$^-$ is observed, implying that a Peierls distortion occurs in this large-U system.

INTRODUCTION

Quarter-filled band "large-U" TCNQ salts, of which Quinolinium Ditetracyanoquinodimethanide [Qn(TCNQ)$_2$] is a well-known example, have been among the most controversial of organic quasi-one-dimensional conductors. By "large-U" we mean that the on-site Coulomb interaction dominates all other interactions of the conduction electrons. The dc conductivity of these materials[1] increases rapidly with temperature, reaching a plateau a little below 300K beyond which it decreases with further temperature increase. Models that have been proposed to account for the properties of these materials include: (1) disorder-induced localization models,[2] (2) a random barrier model,[3] (3) a model that these materials are essentially semiconductors at all temperatures[1], and (4) a model including thermally generated and chemically induced solitons.[4]

In this paper we present measurements of the optical absorption by Qn(TCNQ)$_2$ which show that this compound is a semiconductor on account of a Peierls distortion in the system. At low temperature the gap is comparable to that inferred from the dc conductivity.

EXPERIMENTAL DETAILS

Because the crystals were too small for reflectance studies, absorption measurements were made on composite samples prepared by grinding and mixing many small crystals with an insulating host and compressing the mixture into a pellet. The typical crystal size in these samples was several microns while the volume fraction of the mixture was below 0.01. Thus the crystals were isolated in the host; the effective absorption coefficient could be determined after correcting for the absorption and reflection of the host. In the frequency range studied (below 4000 cm^{-1}) this absorption is mostly due to light polarized along the TCNQ chain direction.

RESULTS

Absorption coefficients versus frequency for $Qn(TCNQ)_2$ are shown in Fig. 1. The absorption is quite low at 100 cm^{-1} but rises by a factor of 30 by 3000 cm^{-1}. Note that there is a change of temperature dependence, with increasing absorption when temperature

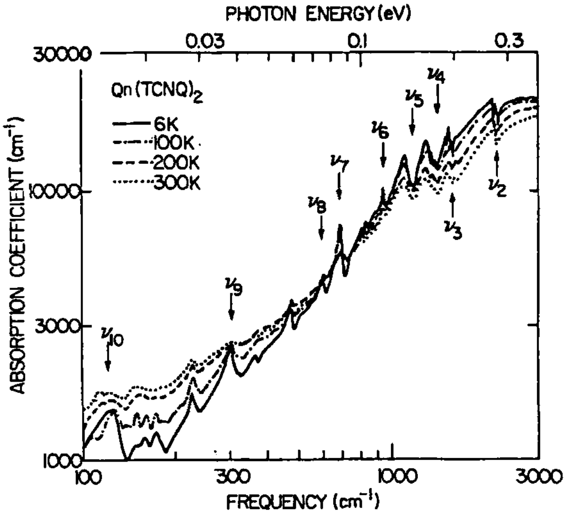

Fig. 1. Absorption coefficient versus frequency for $Qn(TCNQ)_2$. Note the logarithmic scales.

increases for frequencies below 700 cm^{-1} but a reduction at higher frequencies. The structure in the absorption coefficient is caused by vibrational effects, the strongest of which are associated with the a_g totally symmetric modes of $TCNQ^-$. The arrows in Fig. 1 mark the frequencies of 9 of these modes.

DISCUSSION

The presence of the a_g modes in the infrared spectrum is direct evidence that a Peierls distortion (i.e. a charge density wave or dimerization) occurs in $Qn(TCNQ)_2$. It is well known that these modes, normally infrared inactive, become active for polarization along the chain axis due to phase oscillations of a charge density wave.[5] Because of the involvement of the electrons, the oscillator strength associated with these phase phonons is very large. When their frequencies are below the electronic energy gap they appear as ordinary (Lorentzian) resonances whereas when their frequencies overlap the electronic continuum, they have the Fano[6] shape: an antiresonance or dip preceeded by a peak on the low frequency side. Because we observe these a_g modes in the infrared spectrum, we conclude that a Peierls distortion exists in $Qn(TCNQ)_2$.

We know of no other mechanism which could give rise to the observed spectrum. A recent study[7] of the TTF-TCNQ family has shown that as the strength of the $2k_F$ and $4k_F$ scattering in these materials increases, the strength of the a_g modes also increases, direct evidence for the role of the Peierls distortion in the infrared activity of the a_g modes.[7] Disorder will disturb the symmetry of the crystal and lift some selection rules, making some ordinarily infrared inactive modes visible in an infrared spectrum, so that disorder may seem to be a possible explanation. However, the a_g modes are symmetric stretchings of the TCNQ molecule and should remain infrared inactive as long as the molecule retains its shape. Furthermore, disorder would not lead to the enhanced oscillator strength of these modes.

We can obtain an estimate of the magnitude of the Peierls gap in Qn$(TCNQ)_2$ from the lineshape of the a_g modes. We judge that the gap is between 700 and 950 cm^{-1}. The change of shape of the infrared bands is most clearly observed by comparing ν_9 at 305 cm^{-1} with ν_5 at 1195cm^{-1} and ν_4 at 1425 cm^{-1}. The low frequency mode is a peak raised above the background absorption whereas at the frequencies of the higher frequency modes there is a deep dip in the absorption with a peak at the low frequency side. The above range of frequencies agrees with the gap found by fitting the temperature dependence of the conductivity:[1] 2Δ=1200 K or 840 cm^{-1}. Note that these gap estimates also correspond to the frequency of the change in the temperature dependence of the absorption coefficient.

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REFERENCES

1. A.J. Epstein and E.M. Conwell, Solid State Commun. 24, 627 (1977); A.J. Epstein and J.S. Miller, Solid State Commun. 27, 325 (1978); A.J. Epstein, E.M. Conwell and J.S. Miller, Annals of the New York Academy of Sciences 313, 183 (1978).
2. A.N. Bloch, R.B. Weisman and C.M. Varma, Phys. Rev. Lett. 28, 753 (1972); A.A. Gogolin, S.P. Zolotukhin, V.I. Melnikov, E.I. Rashba and T.F. Shchegolev, JETP Lett. 22, 278 (1975).
3. S. Alexander, J. Bernasconi, W.R. Schneider, R. Biller, W.G. Clark, G. Gruner, R. Ohrbach and A. Zettl, Phys. Rev. B 24, 7474 (1981).
4. A.J. Epstein, J.W. Kaufer, H. Rommelmann, I.A. Howard, E.M. Conwell, J.S. Miller, J.P. Pouget and R. Comes, Phys. Rev. Lett. 49, 1037 (1982); M.J. Rice and E. Mele, Phys. Rev. B 25, 1339 (1982); I.A. Howard and E.M. Conwell, Phys. Rev. B 27, 6205 (1983).
5. M.J. Rice, Phys. Rev. Lett. 37, 36 (1976).
6. V. Fano, Phys. Rev. 124, 1866 (1961).
7. C.S. Jacobsen, I.B. Johannsen, and K. Bechgaard, Phys. Rev. Lett. 53, 194 (1984).