irradiation of the crystal with visible light, presumably a photoionization effect. This suggests the possibility of accelerating the decoration process by long-wavelength irradiation. It would also appear that any effect of internal print-out on the plastic yield stress of silver chloride crystals would initially be relatively small, but would increase greatly as the silver migrated to the dislocations. Miller,[4] in this laboratory, has indeed found that the initial hardening is only slight; experiments are now under way to investigate the effects of aging.

Among the experiments suggested by this decoration technique are studies of possible internal dislocation sources and stress-induced pileups in silver chloride. Since any slow room temperature recovery is expected to be arrested at an early stage in the decoration process, it should be possible to study the dislocation distributions resulting from plastic deformation without the necessity of an intervening opportunity for their rearrangement.

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[1] See, for example, J. T. Bartlett and J. W. Mitchell, Phil. Mag. 5, 445 (1960); and S. Amelinckx, Phil. Mag. 3, 307 (1958).

[2] J. W. Castle, J. Appl. Phys. 28, 743 (1957).

[3] P. Suptitz, Z. wiss. Photographie 53, 201 (1959).

[4] M. Miller (to be published).

ELECTRONIC CONDUCTION AND EXCHANGE INTERACTION IN A NEW CLASS OF CONDUCTIVE ORGANIC SOLIDS

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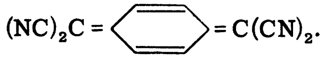
A group of highly conductive organic solids which offer a unique opportunity for experimental study of electronic conduction and interaction in solids has recently been discovered in this laboratory. These materials are salts of the radical-anion formed by addition of an electron to tetracyanoquinodimethan (TCNQ):



TCNQ

In combination with a variety of cations, the $[\mathrm{TCNQ}\cdot]^-$ radical-anion forms two series of salts having the compositions

$$M^+[\mathrm{TCNQ}\cdot]^- \text{ and } M^+[\mathrm{TCNQ}\cdot]^-[\mathrm{TCNQ}]^0,$$

respectively.[1] In both types of salt the band formed from the lowest normally unfilled molecular orbital of the TCNQ is partially filled, being half filled for the first series of salts and one-quarter filled for the second. As a result of the relatively weak intermolecular interactions characteristic of molecular crystals, this band will be quite narrow. In addition, both the bandwidth and the exchange coupling of the odd electrons[2] appear to be strongly influenced by the nature of the cation M^+, and by whether or not $[\mathrm{TCNQ}]^0$ is present in the crystal.

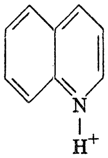
In the quinolinium salt (see Table I), the electrons of the $[\mathrm{TCNQ}\cdot]^-$ radicals appear to form a conventional degenerate system similar to a metal. This is evidenced by the relatively large electrical conductivity (the largest yet reported for an organic solid), the virtual absence of activation energy for conductivity, and the temperature-independent paramagnetism. The magnitude of the paramagnetic component of the susceptibility corresponds to a density of states at the Fermi surface of 7.5 states/ev molecule, which implies a quite narrow energy band.

In the triethylammonium salt the paramagnetic component of the magnetic susceptibility is given by

$$\chi_P = (2g^2\beta^2N/kT)[3+\exp(J/kT)]^{-1}, \qquad (1)$$

with $J = 0.041$ ev. This corresponds to an assembly of N quasi-molecules, each having a triplet state lying at an energy J above a singlet ground state. A single sharp absorption line is observed in the electron spin resonance spectrum at $g = 2.002$.[2] The temperature dependence of the intensity of this line also follows Eq. (1). The

Table I. Electronic properties of representative radical-anion salts.

	Electrical conductivity		Magnetic susceptibility	
Material	Value at 300°K (ohm^{-1} cm^{-1})	Activation energy (ev)	Value at 300°K ($emu\text{-}mole^{-1}$)	Temperature dependence
 $[TCNQ\cdot]^-[TCNQ]^0$	100[a]	<0.01	$+2.2\times10^{-4}$	Decreases gradually to $+1.0\times10^{-4}$ at 77°K
$[(C_2H_5)_3NH]^+[TCNQ\cdot]^-[TCNQ]^0$	4.0[a]	0.14	$+6.4\times10^{-4}$[b]	Eq. (1) with $J=0.041$ ev
$K^+[TCNQ\cdot]^-$	1.9×10^{-4}[c]	0.36	-1.3×10^{-4}	Temperature independent from 77° to 450°K[d]

[a] In direction of highest conductivity (see text).

[b] Paramagnetic contribution.

[c] Measured on compressed powder sample.

[d] $J\sim0.15$ ev from temperature dependence of spin resonance.

electrical conductivity of this salt is highly anisotropic, having room-temperature values of 4.0, 0.05, and 0.001 $ohm^{-1}cm^{-1}$ in the three principal crystal directions and varies exponentially with temperature with an activation energy of 0.14 ev, which is isotropic within experimental error. Preliminary crystallographic results show that this salt belongs to the monoclinic $C2$ space group with four formula units per unit cell. The TCNQ units appear to be arranged in infinite face-to-face stacks with the direction of highest conductivity lying along these stacks and approximately normal to the planes of the TCNQ molecules. The thermoelectric power is -100 $\mu v/°C$ in the direction of highest conductivity, which indicates that electrons are the majority carriers in this material. We have been unable to detect a Hall voltage in this salt and estimate that such a voltage would have been observed if the electron mobility had been greater than 0.04 cm^2/v-sec.[3] A lower limit for the electron mobility of 0.02 cm^2/v-sec can be calculated from the observed conductivity and the assumption that all of the electrons of the radical-anions participate in carrying current.

The final example in Table I, $K^+[TCNQ\cdot]^-$, provides a case in which there is a very low electrical conductivity and a relatively high activation energy for conductivity. The magnetic susceptibility is negative and temperature dependent although there are indications from spin resonance measurements of a triplet level lying ~0.15 ev above the ground state.

We are currently studying a wide range of solids containing $[TCNQ\cdot]^-$ radical-anions and will report on these in detail elsewhere.

We wish to acknowledge the assistance of Dr. Paul Arthur, Jr. in providing us with preliminary results from his crystallographic studies on some of these materials.

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[1] D. S. Acker et al., J. Am. Chem. Soc. (to be published).

[2] D. B. Chesnut, H. Foster, and W. D. Phillips, J. Chem. Phys. (to be published).

[3] It is possible that charge carrier motion in these materials takes place by an activated hopping process, in which case it is questionable whether a Hall effect should be observed; see discussion in J. Phys. Chem. Solids 8, 50 (1959).