ELECTRICAL CONDUCTIVITY AND E.P.R. SIGNAL IN POLYMERIC MATERIALS COMPOSED OF MOLECULES WITH CONJUGATED DOUBLE BONDS

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Numerous experimental studies have established that samples of polymers composed of molecules with conjugated double bonds have the following remarkable properties:

1) Their electrical conductivity is several orders greater than that of organic dielectrics and in a number of cases, it is comparable with the electrical conductivity of ordinary semiconductors. The electrical conductivity of samples usually depends on temperature according to the law $\exp(-E/kT)$ where E is 1-10 eV [1]; in some cases it is apparently independent of temperature.

2) Such materials give a narrow line for the electron paramagnetic resonance (e.p.r.) signal, usually without a hyperfine structure and with a g-factor close to 2 [1, 2]. The e.p.r. signal corresponds to the effective number of unpaired electrons (free spins), which varies over a very wide range and may reach $10^{18}-10^{17}$ per g of material in some cases.

At present there have been insufficient systematic measurements of the electrical conductivity and particularly of the mobility of carriers and properties of the e.p.r. signal for the same samples. It is therefore impossible to maintain that the free spins are identical to the electrons which move along the sample molecules and are the current carriers.

However, it is expedient to study the properties of a model of the material which is based on the following assumptions: 1) The quite long polymeric molecules with conjugated double bonds have an energy spectrum with bands of permissible energies; and 2) the band of permissible energies contains quasifree electrons (or holes) which form a degenerate gas.

Similar "metallic" models of molecules were used successfully in the examination of the spectra of polyene molecules [3]. As the electron gas is unidimensional within the framework of the given model, the condition for the degeneration of the gas has the form $n \gg 2(2mkT)^{1/2}\pi\hbar$ where n is the number of electrons per linear centimeter of the conducting molecule. This condition is satisfied by the presence of one free electron for several atoms in the conjugation chain.

Let us first examine the problem of the conductivity of the sample within the framework of the proposed model. It will be determined, on the one hand, by the nature of the movement of electrons along the molecules, and, on the other hand, by the probability of the transfer of electrons from one molecule to another. In this article we will limit ourselves to discussion of the first process.

If a molecule, namely, a linear metallic conductor, is oriented along the direction of the applied constant electric field F, an electric current is produced in it. In this case there are two sources of resistance: The longitudinal thermal vibrations of the atoms in the "lattice" and the presence of heterogeneities in it. In calculating the scattering of the electrons by the thermal vibrations in a molecule, we may limit ourselves to a low-temperature approximation as always $h\omega \gg kT$, where ω_0 is the characteristic vibration frequency of the molecule.

In the case of a unidimensional conductor, the scattering of electrons on the phonons has a character different from that of normal scattering in a three-dimensional crystal. In particular, in the unidimensional case, the law of the conservation of the quasiimpulse has a scalar and not a vector character. In the case when the electron energy is quadratically dependent on the quasiimpulse, only phonons with a quasiimpulse

$$q = -2f,$$

where f is the electron quasiimpulse, may scatter electrons (neglecting transfer processes).

This means that as low-angle scattering is impossible, the electrons must only be scattered backwards. The number of phonons with a quasiimpulse q is very low at low temperatures. Therefore, the resistance to the movement of an electron along a molecule, resulting from scattering at thermal vibrations, is extremely low. Calculations using the normal scheme and a kinetic equation gives the following expression for the electrical conductivity:

$$\sigma = \frac{e^2 Mu\,(dE_*/df)^2}{16\pi a\hbar^2 C^2 f_*}\, e^{\theta_*/T}\,.$$

Here a is the interatomic distance, u the effective velocity of sound in the chain of atoms, M the mass of the elementary cell, and $\theta_* = 2\hbar u f_*/k$, with the asterisk denoting that the values refer to conditions when $E = \zeta$, where ζ is the partial potential of the electron gas (Fermi level).

The low probability of scattering on the phonons in the chain leads to an exponentially high value for the electrical conductivity. In the case of a low concentration of free electrons when there is no degeneration, the conductivity has a normal activation character.

Reaction	Relaxation time (sec)	
	In a three-dimensional crystal	In a unidimensional crystal
With transverse phonons	10^{-2}	10^{-2}
With longitudinal phonons	10^{-4}	–
With nuclear spins	10^{-4}	10^{-4}
Spin–spin	10^{-3}	–
Spin–current	10^{-7}	–
With impurities	10^{-2}	10^{-2}

Another possible source of electron scattering in the chain is a reaction with impurities. In the given case, by impurities we mean any disruption of the regular periodicity, for example, as a result of the existence of side groups in a linear molecule or a break in the regular sequence of single and double bonds. As scattering by impurities cannot be regarded as a small perturbation in a unidimensional chain, we should use the known theory of strong local perturbations to calculate the probability of scattering [4].

If we introduce the symbols: V_0, the deviation of the potential energy from its value when no defects exist, $1/d$, the number of defects per unit length and ε_1, the first coefficient of the expansion of the unperturbed energy in a Fourier series, then

$$w(f) = \frac{1}{1 + (2\varepsilon_1 \sin fa/V_0)^2}$$

may be written for the probability of scattering [4].

The value

$$\sigma = \frac{e^2 d}{\pi\hbar}\left[\frac{2\varepsilon_1 \sin \pi na/2}{V_0}\right]^2$$

is obtained with the normal kinetic equation for electrical conductivity.

The value for the conductivity obtained from the last formula does not depend on temperature and corresponds to the upper limit of conductivity for a unidimensional chain.

Let us now examine the characteristics of the e.p.r. line within the framework of the proposed molecular model. In metals the e.p.r. lines are known to be very wide because of the spin-orbital interaction and Elliott [5] showed that the width of the e p.r. line is proportional to the conductivity of the metal. The corresponding relaxation time τ was found to equal $\tau \sim 10^{-9}$ sec. However, this conclusion is not applicable to a unidimensional metal. The spin-orbital interaction operator has the form

$$H' \sim (\nabla V \times \mathbf{p}),$$

where V is the potential energy of an electron in the metal and **p**, its impulse. Evidently, $H' = 0$ in the unidimensional case.

Overhauser calculated other possible relaxation mechanisms which lead to broadening of the e.p.r. line [6].

The table shows that all these mechanisms correspond to considerably greater relaxation times in the three-dimensional metal than does the spin-orbital reaction mechanism, and therefore these mechanisms do not appear in ordinary metals. As no spin-orbital reaction appears in a unidimensional crystal, we should consider other possible relaxation mechanisms. The table gives the results of our investigations.

The Hamiltonian corresponding to the interaction of the electron spin with the electrical field formed as a result of the longitudinal vibration of the atoms of the chain, the spin–spin interaction, and the interaction of the spin of the given electron with the current, associated with the movement of other electrons, reduces to zero in the unidimensional case.

The table also gives the relaxation times calculated for other possible mechanisms in the unidimensional case.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.