Physical Chemistry

Corresponding Member of the Academy of Sciences of the USSR V. G. Levich, V. S. Markin, Yu. G. Chirkov

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Abstract

Full Text

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On Electrical Conductivity and the E.P.R. Signal in Polymeric Materials Built from Molecules with Conjugated Double Bonds

It has been established in numerous experimental works that samples of polymers built from molecules with conjugated double bonds exhibit the following remarkable properties:

1) They possess an electrical conductivity several orders of magnitude greater than the electrical conductivity of organic dielectrics and, in a number of cases, comparable with the electrical conductivity of ordinary semiconductors. The electrical conductivity of the samples usually depends on temperature according to the law $\exp(-E/kT)$, where the quantity E is 1-10 eV (1); in some cases it apparently does not depend on temperature.
2) In such substances a narrow line of the electron paramagnetic resonance (e.p.r.) signal is observed, usually without hyperfine structure and with a g-factor close to 2 (1, 2). The e.p.r. signal corresponds to an effective number of unpaired electrons (free spins) varying within very wide limits, reaching in some cases 10^{18}-10^{17} per 1 g of substance.

At present there are insufficient systematic measurements of electrical conductivity and especially of carrier mobility and of the properties of the e.p.r. signal for the same samples. Therefore it cannot be asserted that the free spins are identical with the electrons moving along the molecules of the sample and serving as current carriers.

It seems, however, expedient to investigate the properties of a model of the substance based on the following assumptions: 1) sufficiently long polymer molecules with conjugated double bonds possess an energy spectrum with bands of allowed energies; 2) in the band of allowed energies there are quasi-free electrons (or holes), forming a degenerate gas.

Similar "metallic" models of molecules have been successfully applied to the consideration of the spectra of polyene molecules (3). Since the electron gas within this model is one-dimensional, the condition for degeneracy of the gas has the form $n \gg 2(2mkT)^{1/2}/\pi\hbar$, where n is the number of electrons per 1 linear centimeter of the conducting molecule. This condition is satisfied when there is one free electron for several atoms in the conjugation chain.

Let us first consider the question of the conductivity of a sample within the framework of the proposed model. It will be determined, on the one hand, by the character of the motion of electrons along the molecules and, on the other hand, by the probability of transition of electrons from one molecule to another. In the framework of this article we shall confine ourselves to discussion of the first process.

If a molecule—a linear metallic conductor—is oriented along the direction of the applied constant electric field F, then an electric current arises in it. In this case there are two sources of resistance: longitudinal thermal vibrations of the atoms in the "lattice" and the presence of inhomogeneities in it. In calculating the scattering of electrons by

in thermal vibrations in the molecule one may restrict oneself to the low-temperature approximation, since always $\hbar\omega \gg kT$, where ω_0 is the characteristic vibrational frequency of the molecule.

In the case of a one-dimensional conductor, electron scattering by phonons has a character different from ordinary scattering in a three-dimensional crystal. Namely, the law of conservation of quasimomentum in the one-dimensional case has a scalar, not a vector, character. In the case when the electron energy depends quadratically on the quasimomentum, only phonons with quasimomentum

$$q = -2f,$$

where f is the electron quasimomentum, can scatter an electron (disregarding umklapp processes).

This means that, since scattering through a small angle is impossible, the electron must be scattered only backward. At low temperatures the number of phonons with quasimomentum q is very small. Therefore the resistance to the motion of an electron along the molecule, associated with scattering by thermal vibrations, is very small. A calculation by the usual scheme using the kinetic equation leads to the following expression for the electrical conductivity:

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

Here a is the interatomic distance; u is the effective velocity of sound in the chain of atoms; M is the mass of the elementary cell; $\theta_* = 2\hbar u f_*/k$; the asterisk indicates that the value of the corresponding quantities is taken at $E = \zeta$, where ζ is the partial potential of the electron gas (the Fermi level).

The small probability of scattering by phonons in the chain leads to an exponentially large value of the electrical conductivity. In the case of a low concentration of free electrons, when degeneracy is absent, the conductivity has the usual activation character.

Another possible source of scattering of electrons in the chain may be interaction with impurities. By impurities in the present case is meant any violation of the proper periodicity—for example, due to the existence in the linear molecule of side groups or a violation of the regular alternation of single and double bonds. Since scattering by an impurity in a one-dimensional chain cannot be regarded as a small perturbation, to compute the scattering probability one should use the known theory of local strong perturbations (^{4}).

If we introduce the notation: V_0 is the deviation of the potential energy from its value in the absence of a defect; $1/d$ is the number of defects per unit length; and ε_1 is the first coefficient in the expansion of the unperturbed energy in a Fourier series, then for the scattering probability one may write (^{4})

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

With the aid of the usual kinetic equation, for the electrical conductivity one obtains the value

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

The value of the conductivity given by the last formula does not depend on temperature and corresponds to the upper limit of the conductivity of a one-dimensional chain.

Let us now turn to a discussion of the features of EPR lines within the framework of the proposed molecular model. As is known, in metals EPR lines have a large width caused by spin-orbit interaction. Elliott (^{5}) showed that the width of the EPR line is proportional to the conductivity of the metal. The corresponding relaxation time τ turns out to be

equal to $\tau \sim 10^{-9}$ sec. This conclusion is not applicable, however, to a one-dimensional metal. The spin-orbit 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 $\mathbf{p}$ is its momentum. In the one-dimensional case, obviously, $H' = 0$.

Other possible relaxation mechanisms leading to broadening of the e.p.r. line were calculated by Overhauser ^{6}.

Table

Interactions	Relaxation time (sec), in a three-dimensional crystal	Relaxation time (sec), in a one-dimensional 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}

It is seen from the table that all these mechanisms correspond, in a three-dimensional metal, to relaxation times substantially longer than the spin-orbit interaction mechanism; therefore they are not manifested in ordinary metals. Since in a one-dimensional crystal the spin-orbit interaction is not manifested, other possible relaxation mechanisms should be taken into account. The results of such a consideration are given in Table 1.

The Hamiltonian corresponding to the interaction of the electron spin with the electric field arising as a result of longitudinal vibrations 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 motion of other electrons, in the one-dimensional case becomes zero.

The table also gives the relaxation times calculated for other possible mechanisms in the one-dimensional case.

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