Electrical Conductivity of One-Dimensional Conductors

H R. Zeller
Brown Boveri Research Center, CH-5401 Baden, Switzerland
(Received 23 February 1972)

It is shown that the model of interrupted strands offers a simple explanation for the temperature dependence of one-dimensional conductors. An array of small metallic particles is used to simulate the essential properties of the model.

One-dimensional conductors differ in many respects and in a nontrivial way from three-dimensional conductors. Many theoretical papers were devoted to the study of such systems, but not until recently has it become possible to find examples of pseudo–one-dimensional metals and to compare experimental results with theoretical predictions. The best known one-dimensional conductors[1] are the tetracyanoquinodimethan (TCNQ) salts and the mixed-valency planar complexes of Pt [for example, $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$].

The TCNQ charge-transfer salts form linear chains of TCNQ molecules stacked face to face.[1] Highly polarizable donor molecules, such as *N*-methyl phenazinium (NMP) in the case of the NMP-TCNQ salt, transfer an electron to each TCNQ molecule. This results in a half-filled conduction band and the possibility of one-dimensional conductivity along the TCNQ chains. The mixed-valency planar Pt complexes[2] on the other hand form linear chains of Pt atoms with a Pt-Pt distance close to the Pt-Pt distance in Pt metal. Partial oxidation of the divalent Pt (in the above-mentioned example with 0.3 Br) results in a stable compound with a fractional valency or, in a band-structure picture, a partially filled band. The highest occupied Pt band (probably d_{z^2}) is only partially filled and one-dimensional metallic conductivity becomes possible.

Although the TCNQ salts and the Pt complexes are completely different in their chemistry and electronic structure, they are very similar in their physical properties. In particular, the dc electrical conductivity has many common features: a high-temperature region where the electrical conductivity is roughly temperature independent and a low-temperature region where the electrical conductivity is thermally activated. In this region there is no single activation energy [curves of $\log\sigma$ versus $1/T$ flatten out at low temperatures] but by trial and error one finds $\log\sigma \sim T^{-\mu}$ with $\frac{1}{3} \leq \mu \leq \frac{1}{2}$.[3-5]

Three different models have been proposed to describe the physical properties of one-dimensional conductors. Epstein *et al.*[6] discussed the TCNQ salts in terms of the one-dimensional Hubbard model. Although the assumption of a transition from a high-temperature metallic state to a low-temperature Mott insulator is consistent with several experimental observations, it fails to explain the observed temperature dependence of the electrical conductivity.[7] Furthermore, in the case of $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ a metal-to-insulator transition would, for chemical reasons,[2] result in 15% of the Pt atoms in the chain being tetravalent, the others being divalent. A Mössbauer study[8] showed that all of the Pt is equivalent at 4.2°K.

The two other models emphasize the effects of disorder and imperfections in the real crystal. In both models the starting point is an ideal crystal consisting of an array of linear parallel strands. According to simple band theory[2] the partially filled one-dimensional band should result in one-dimensional metallic conductivity. In the real crystal this picture is changed in a nontrivial way by the presence of disorder and defects: (i) Interruptions of the Pt chains by defects such as vacancies or impurities localize the electrons within the resulting chain segments.[9,10] (ii) Weak random potentials also lead to a localization of the conduction electrons in a one-dimensional system.[11] In the case of $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ such potentials are provided by the statistical occupancy of available K and Br sites.[2-4]

In the interrupted-strand model,[9,10] which applies when the mean distance between interruptions l_0 is smaller than the localization length L_0 resulting from the random potentials, the electron states are standing Bloch waves. In the weak-localization model (WL),[3,4] the electron states are still Bloch states because the strong potential is periodic, but of finite extension as a result of the effect of the weak random potentials. This model applies for $L_0 < l_0$.

Recent experiments on $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$ show that $\sigma_\parallel$ and $\sigma_\perp$, the electrical conductivities parallel and perpendicular to the strands, have

the same temperature dependence.[5] Furthermore, $\sigma_{\parallel}(300°K)$ differs very much from crystal to crystal while $\sigma_{\perp}(300°K)$ shows no measurable variation. From this we conclude that the limiting step in conductivity is an interstrand transition and that $\sigma_{\parallel}$ is determined by $\sigma_{\perp}$ and the average length l_0 of a strand segment. This does not rule out the WL model, but it rules out the one-dimensional mechanism for the conductivity proposed in Refs. 3 and 4.

In the following we will discuss the temperature dependence of the dc conductivity in terms of the interrupted-strand model assuming quasifree electrons in the strand segments. However, we would like to point out that similar arguments can be constructed based on the WL model.

First we consider a single segment at $T=0$. Since the wave functions have to have nodes at the boundaries, only a discrete set of $\vec{k}$ values is allowed and the resulting splitting ΔE_k of the energy levels is

$$\Delta E_k = v_F/l_0.$$

Estimating the Fermi velocity v_F to be $\sim 10^8$ cm/sec and $l_0 \sim 300$ Å, we obtain a value of $\sim 2.2\times 10^{-2}$ eV for ΔE_k. Another important consequence results from the fact that electronic charge is quantized.[12] If a capacitor is discharged, its two plates exchange electrons until their chemical potentials μ are equal. Since electronic charge is quantized, there always remains a residual mismatch $\Delta\mu \leq e/2C$ (e is the electron charge; C, capacitance) which in macroscopic capacitors is negligible. Although the picture of viewing a strand segment as a cylindrical capacitor is oversimplified, the same arguments apply and in the ground state there is a distribution of chemical potentials. The width of the distribution is of the order of the energy required to add an electron to a neutral strand. Ultimately the smearing results from a slight difference in work function between different strand segments due to frozen-in charges, polarizations, impurities or the statistical occupancy[2] of available K and Br sites in $K_2Pt(CN)_4Br_{0.3}\cdot 3(H_2O)$. The strands can only partially balance this difference due to the discreteness of electronic charge. Such a model has been successfully applied to the description of tunnel junctions containing small metal particles in the oxide.[12]

Next we discuss the conditions for current flow. It is clear that the fixed number of electrons on each strand segment results in an insulating ground state.[12] In order to obtain a current flow, we have to change the electron occupation number on the strand segments by at least one. As in the case of small metal particles,[12] this requires an activation energy. In a capacitor model the electrostatic energy required to add an extra electron to a strand is

$$E_C = e^2/2C + (2e/C)\textstyle\sum_i C_i \Delta\mu_i,$$

where C denotes the total capacitance, C_i the capacitance between the strand and an adjacent strand i and $\Delta\mu_i$ the difference in chemical potential between the strand and strand i. We estimate E_C to be of the order of 10^{-2}–10^{-1} eV. This argument is not necessarily connected to the oversimplified capacitor model. A more general treatment, such as the one applied by Mezei[13] to the small-metal-particle problem, is possible.

The elementary excitation for current transport consists in transferring one electron from one strand segment to another, starting from the ground state. Once such an excitation is created, the "electron-hole pair" cannot move freely but has a thermally activated mobility due to the distribution of activation energies. Each excitation polarizes the surrounding chains, changing the $\Delta\mu$ between neighboring strand segments. Thus the problem of calculating conductivity versus temperature gets extremely complicated. One has a distribution of activation energies, and changing the occupation number of a strand segment affects the distribution of chemical potentials on adjacent strands. It is possible, however, to avoid all mathematical difficulties by using a modification of the small-metal-particle experiment by Zeller and Giaever[12] as an analog for the one-dimensional conductor. If we introduce, using the techniques described in Ref. 12, instead of only one layer, as Zeller and Giaever did, many layers of small metal particles in a metal-insulator-metal tunnel junction, then this system has all the above discussed properties. The particles are separated by tunnel barriers formed by an oxide layer, the electron levels are quantized, and there is at zero temperature a fixed number of electrons on each particle. The different geometry, nearly spherical particles in one case and one-dimensional strands in the other, is unimportant as long as the conductivity is not affected by the conducitivty within the strand or within the particle, respectively, and as long as only nearest-neighbor tunneling is considered. Furthermore we consider only the situation where the applied voltage across a tunnel barrier is small compared to kT/e, i.e., the

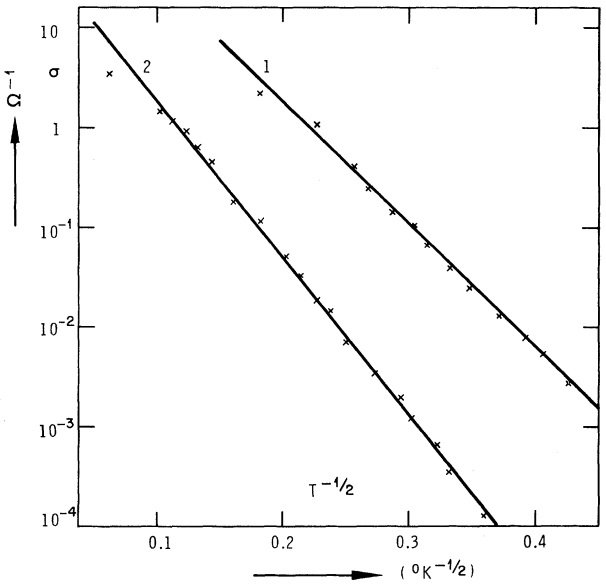

FIG. 1. Temperature dependence of the zero-bias conductivity of a Sn-Sn tunnel junction containing ten layers of small tin particles in the oxide. The particles were formed by vapor depositing a small amount of Sn and oxidized by exposing the junction to air after each evaporation step in junction 1 for 30 min and junction 2 for 2 h. The average particle radius is about 40 Å in both junctions.

zero-bias conductivity. For only one layer of particles, the model outlined above is solvable and one finds quantitative agreement between theory and experiment for the voltage and temperature dependence of the conductivity.[12,13]

We have fabricated junctions consisting of two crossed Sn strips with ten layers of particles in between, using the techniques of Ref. 12. After each evaporation step the junctions were oxidized in air at 20°C for a constant time ranging from 30 min to 24 h. The junction area was about 1 mm^2. On such junctions the temperature dependence of the conductivity has been measured. In order to avoid voltage effects, the applied voltage has to be small compared to kT/ne (n is the number of particle layers). Around and below T_c of bulk Sn we observed superconductivity effects, analogous to those of Ref. 12. Apart from that, the low-temperature conductivity of the small-particle system varies as $\log\sigma \sim T^{-\mu}$ with $\mu \approx \frac{1}{2}$, as shown in Fig. 1. Thus the small-particle system reproduces the general properties of the temperature dependence of σ in a one-dimensional conductor. It is interesting to note that in the small-particle system only tunneling between adjacent particles takes place.[12] Thus the $\log\sigma \sim T^{-\mu}$ law exclusively results from the distribution of activation energies.

If one applies the formalism by Mott[14] and Ambegaokar, Halperin, and Langer[15] to the rate of interstrand transitions, a $\log\sigma \sim T^{-1/3}$ law results due to the fact that the problem is two-dimensional.[5] In this model the departure from the $\log\sigma \sim T^{-1}$ law stems from optimizing tunneling distance versus effective activation energy. At low temperature it is more favorable for an electron to tunnel to a more distant strand with a correspondingly smaller activation energy. If the tunneling distance is kept constant, the formalism of Refs. 14 and 15 predicts a simple $\log\sigma \sim T^{-1}$ law. Thus it is not clear whether the dominant factor in producing the $\log\sigma \sim T^{-\mu}$ ($\frac{1}{3} \leq \mu \leq \frac{1}{2}$) law in one-dimensional conductors is the mechanism described by Mott[14] and Ambegaokar, Halperin, and Langer[15] or merely the distribution of activation energies as in the small-particle system.[16]

In the WL model[3,4] disorder in the crystal also causes a distribution of activation energies for interstrand tunneling, and we would expect a similar temperature dependence of the electrical conductivity. The determination of the nature of the electronic states in one-dimensional conductors therefore requires further experimental and theoretical investigations.

It is a pleasure to acknowledge many stimulating discussions with Dr. J. Bernasconi, Dr. M. J. Rice, and Dr. S. Strässler.

[1]For a review see I. F. Schchegolev, to be published.
[2]K. Krogmann, Angew. Chem., Int. Ed. Engl. 8, 35 (1969).
[3]A. N. Bloch, R. B. Weismann, and C. M. Varma, Phys. Rev. Lett. 28, 753 (1972).
[4]J. H. Perlstein, M. J. Minot, and V. Walatka, to be published.
[5]J. Bernasconi, D. Kuse, M. J. Rice, and H. R. Zeller, to be published.
[6]A. J. Epstein, S. Etemad, A. F. Garito, and A. J. Heegar, Phys. Rev. B 5, 952 (1972).
[7]R. A. Bari and T. A. Kaplan, Bull. Amer. Phys. Soc. 17, 358 (1972).
[8]W. Rüegg, D. Kuse, and H. R. Zeller, to be published.
[9]D. Kuse and H. R. Zeller, Phys. Rev. Lett. 27, 1060 (1971).
[10]M. J. Rice and J. Bernasconi, Phys. Lett. 38A, 277 (1972).
[11]R. E. Borland, Proc. Phys. Soc., London 78, 926 (1961); E. N. Economou and M. H. Cohen, Phys. Rev. B 4, 396 (1971).

[12]H. R. Zeller and I. Giaever, Phys. Rev. 181, 789 (1969).
[13]F. Mezei, Phys. Rev. B 4, 3775 (1971).
[14]N. F. Mott, Phil. Mag. 19, 835 (1969).
[15]V. Ambegaokar, B. I. Halperin, and J. S. Langer, Phys. Rev. B 4, 2612 (1971).
[16]A distribution of activation energies can only produce a deviation from $\log\sigma \sim T^{-1}$ at not too low temperatures.

Theory of Surface Magnetoplasmons in Semiconductors*

J. J. Brion and R. F. Wallis
University of California, Irvine, California 92664

and

A. Hartstein and E. Burstein
University of Pennsylvania, Philadelphia, Pennsylvania 19104

(Received 13 April 1972)

A theory of surface magnetoplasmons in semiconductors is developed with the inclusion of retardation for the geometry in which the magnetic field is parallel to the surface and the direction of propagation is perpendicular to the magnetic field. If the background dielectric constant ϵ_∞ lies in a suitable range for a given value of the magnetic field, gaps appear in the dispersion relation for the surface magnetoplasmons. The possible experimental observation of these gaps is discussed.

The dispersion curve for surface polaritons associated with surface plasmons in n-type InSb has recently been observed by Marschall, Fischer, and Quiesser[1] using the anomalies introduced into the infrared reflectivity by a grating ruled on the surface. At large wave vectors ($k \gg \omega_p/c$) the dispersion curve approaches the asymptotic value $\omega_{sp} \equiv \omega_p(1+1/\epsilon_\infty)^{-1/2}$, where ω_p is the bulk plasma frequency defined by $(4\pi ne^2/m^*\epsilon_\infty)^{1/2}$, n is the free-carrier concentration, m^* is the effective mass, and ϵ_∞ is the high-frequency–background dielectric constant. At small wave vectors ($k < \omega_p/c$) the dispersion curve lies just to the right of the light line $\omega = kc$ and joins the light line at $\omega = 0$.

It is of interest to consider the effects which may arise when an external magnetic field is applied. Chiu and Quinn[2] have investigated this problem for a metal taking $\epsilon_\infty = 1$, a case which does not reveal the interesting effects reported in the present paper. We have developed the theory of surface magnetoplasmons including retardation for the case of semiconductors such as n-type InSb, where the energy band is to a good approximation simple and spherical, and $\epsilon_\infty \gg 1$. The analysis becomes particularly simple in the geometry where the external magnetic field is parallel to the surface and the direction of propagation is perpendicular to the magnetic field, so we restrict ourselves to this case. The material is assumed to be semi-infinite and to fill the half-space specified by $x \geq 0$. The external magnetic field B_0 is taken in the y direction and the wave vector in the z direction. The dielectric tensor has the form

$$\begin{pmatrix} \epsilon_1 & 0 & -i\epsilon_2 \\ 0 & \epsilon_3 & 0 \\ i\epsilon_2 & 0 & \epsilon_1 \end{pmatrix},$$

where $\epsilon_1 = \epsilon_\infty[1+\omega_p^2/(\omega_c^2-\omega^2)]$, $\epsilon_2 = \epsilon_\infty\omega_c\omega_p^2/\omega(\omega^2-\omega_c^2)$, $\epsilon_3 = \epsilon_\infty(1-\omega_p^2/\omega^2)$, and $\omega_c = eB_0/m^*c$. The present case involving a gyrodielectric tensor is formally similar to the case of a magnetic medium with a gyropermeability tensor.[3] Both cases exhibit nonreciprocal effects—a lack of equivalence of positive and negative wave vectors.

Our starting point is Maxwell's equations. After we eliminate the magnetic field from the curl equations, we obtain

$$\text{curl}\,\text{curl}\vec{E} + (1/c^2)\partial^2\vec{D}/\partial t^2 = 0, \tag{1}$$

where $\vec{E}$ is the electric field and $\vec{D}$ is the displacement. We seek solutions of the form

$$\vec{E} = (E_{ix}, 0, E_{iz})e^{-\alpha x}e^{i(kz-\omega t)}, \quad x \geq 0, \tag{2a}$$

$$\vec{E} = (E_{0x}, 0, E_{0z})e^{\alpha_0 x}e^{i(kz-\omega t)}, \quad x < 0. \tag{2b}$$

Equations (2) form a nontrivial solution to Eq. (1) only if

$$\alpha^2 = k^2 - (\omega^2/c^2)\epsilon_V, \tag{3a}$$

$$\alpha_0^2 = k^2 - \omega^2/c^2, \tag{3b}$$