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MODELLING OF THE BEHAVIOUR OF HOPPING CONDUCTIVITY IN A SOLID EXHIBITING A SEMICONDUCTOR-INSULATOR TRANSITION, AS A FUNCTION OF FREQUENCY

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Abstract. We propose a model which explains the evolution of the frequency dependent conductivity while an organized structure appears in an initially amorphous system. We assume that the crystalline organization is connected with the existence of an anisotropy. An anisotropy parameter is calculated. An "a priori" calculation of the conductivity is developed, which correctly accounts for the experimental results obtained on "low temperature" carbons.

Introduction.— The theoretical study of amorphous solids has widely used the concept of localized states bound to the existence of a random potential in these materials. The numbering of sites (donors and acceptors) among which the electrons move in an electric field can be obtained by observing the behaviour of conductivity as a function of frequency (1,2). The interpretation of results thus obtained required an implement of a set of models (3,4) based, for most of them, on the assumption that the solid can be represented by a population of localized states (5). Some authors (6,7) have described the conduction mechanism in these materials by modelling the random path of electrons : thus the hint to create simulations (8) using percolations methods (9). All these models contribute to point out a conductivity law as a function of frequency identical to the experimental law $\sigma(\omega) \sim \omega^s$.

Some works have reported metal-non-metal transitions (2) due to a gradual reorganization of the crystal structure of the compounds. It seems interesting to consider a description of these transitions by trying to establish a correlation between the s exponent, that characterizes the behaviour of conduction as a function of frequency, and the degree of structure organization, measured with the help of an order parameter as described by Landau (10). By doing so, we start from a model, describing the properties of amorphous compounds, which contains parameters capable of introducing gradually the concept of order.

I - Proposed model.— Generally it is considered that the properties of amorphous solids are explained with the help of isotropic models. Thus the way to consider the appearance of an order consists in introducing an anisotropy factor into the crystal structure. The dielectric constant becomes a tensor whose three components ϵ_x , ϵ_y , ϵ_z can be determined. Consequently the potential around an atom must also be anisotropic, which implies that, for a given normal mode the phonons frequency changes according to the considered direction (11), that is v_x , v_y , v_z . For the sake of simplicity, we have supposed that $\epsilon_x = \epsilon_y$ (thus $v_x = v_y$). Thus the dielectric constant anisotropy induces a distortion of equipotential surfaces around a donor site in this model. The surface becomes ellipsoid which large axis, i.e. parallel to Oz , has a length $2a$, and which short axis has a length $2b$, for a given value W , of the energy. W , represents the height of the potential barrier that an electron settled in a donor site at the center of the ellipsoid must overcome to reach a site at a distance R on the ellipsoid. It is due to the coulombian interaction forces (12,13). If we call W_M the energy required to extract an electron from a donor site (3) we obtain : $W_M - W_x = e^2(b\epsilon_x)^{-1}$; $W_M - W_z = e^2(a\epsilon_z)^{-1}$; and along a direction making an angle θ with the Ox axis, $W_M - W_\theta = e^2(R_\theta\epsilon_\theta)^{-1}$, R_θ and ϵ_θ being the values of the radius vector and of the permittivity along the given direction. Obviously, on an equipotential surface, we have : $W = W_R = W_x = W_y$ or $\epsilon_z/\epsilon_x = b/a$. When an electric field $\mathcal{E}$ of circular frequency ω is applied, which direction makes an angle ϕ with the Ox axis, each pair of sites is located by γ (angle with the field direction) and R (distance bet-

ween both sites). Under these conditions, the pairs of sites thus characterized participate to the conductivity. The real part is (14) :

$$\frac{i(\omega)}{\mathcal{E}(\omega)} = \frac{n(\gamma, R) e^2 R^2 \cos^2 \gamma}{4kTch^2(W/2kT)} \cdot \frac{\omega^2 \tau}{1 + \omega^2 \tau^2} \quad (1)$$

$i(\omega)$ represents the current density, $n(\gamma, R)$ is the number of identical pairs of sites and τ is the relaxation time corresponding to electron hop.

Let $dp(R, \gamma)$ be the number of pairs in the elementary volume dV ; generalizing relation (1) leads to the expression of the real elementary conductivity, (assuming that $ch^2(W/2kT) \approx 1(5,14)$):

$$d\sigma'(\omega) = dp(\gamma, R) e^2 R^2 \cos^2 \gamma (4kT)^{-1} \omega^2 \tau (1 + \omega^2 \tau^2)^{-1} \quad (2)$$

Let N_A and N_D be the number of donors and acceptors sites per unit volume, we find the distribution $dp(\gamma, R)$ of the number of pairs in the elementary volume dV : $dp(\gamma, R) = N_A N_D dV$. The quantity dV is the volume determined by the variations $d\theta$ and $d\psi$ (ψ is the angle of rotation of the ellipsoid around the Z axis), and between two equipotential ellipsoidal surfaces, both centered on the donor site and characterized by the semi-axes a and $a + da$. Using the parametric form of the ellipsoid in cylindric coordinates we obtain : $dV = a^2 (\epsilon_z / \epsilon_x)^2 da \sin \beta d\beta d\psi$, where β is related to θ by the equation $a \cos \beta = R \cos \theta$. The appearance of an ordered structure in an initially amorphous solid generally begins by short distance order around localized sites (15). Gradually these sites can be changed into conducting microdomains in which the electronic energy levels can be considered as delocalized (16). However, at the beginning of this evolution, i.e. before the appearance of a long distance order, these organized microdomains are still randomly oriented in the material (2). This phenomenon is taken into account by considering the mean value of $d\sigma'(\omega)$, in the whole space. Thus, we obtain the mean contribution to the conductivity of dipoles which acceptor site is between two homothetic ellipsoidal surfaces centered on the donor site :

$$d\sigma'(\omega) = N_A N_D e^2 (36kT)^{-1} (\epsilon_z / \epsilon_x)^2 \{1 + 2 (\epsilon_z / \epsilon_x)^2\} \omega^2 \tau (1 + \omega^2 \tau^2)^{-1} a^4 da \quad (3)$$

The calculated conductivity $d\sigma'(\omega)$, is the mean contribution to the conductivity of all dipoles characterized by a hopping time between τ and $\tau + d\tau$. The relaxation time in the z direction is : $\tau = v_z^{-1} \exp(2\alpha a)$, where α^{-1} represents the Bohr radius of the localized sites. The value $da = (2\alpha\tau)^{-1} d\tau$, introduced in equation (3) gives the conductivity $\sigma'(\omega)$:

$$\sigma'(\omega) = N_A N_D (72\alpha kT)^{-1} e^2 (\epsilon_z / \epsilon_x)^2 \{1 + 2 (\epsilon_z / \epsilon_x)^2\} \omega \int_0^\infty a^4 \omega \tau (1 + \omega^2 \tau^2)^{-1} d\tau / \tau$$

The integral can be calculated (3,4,5,11) :

$$\sigma'(\omega) = \pi N_A N_D (144 kT)^{-1} e^2 (\epsilon_z / \epsilon_x)^2 \{1 + 2 (\epsilon_z / \epsilon_x)^2\} \omega a_\omega^4,$$

where a_ω is the longer semi-axis of the ellipsoid such that the relaxation time corresponding to the hop from the donor site (at the center of the ellipsoid) to the acceptor site located on the equipotential surface is τ_ω , with along the z direction $\omega \tau_\omega = 1$. The relaxation time previously defined leads to : $\omega = \tau^{-1} = v_z \exp(-2\alpha a_\omega)$. The value of a_ω can thus be evaluated : $a_\omega = (2\alpha)^{-1} \ln(v_z / \omega)$. The investigated expression is written :

$$\sigma'(\omega) = \pi N_A N_D (72kT)^{-1} (2\alpha)^{-5} e^2 (\epsilon_z / \epsilon_x)^2 \{1 + 2 (\epsilon_z / \epsilon_x)^2\} \omega \{\ln(v_z / \omega)\}^4$$

The random orientation of microdomains gives rise to any orientation of the axis of the various ellipsoids that characterize the short distance organization of each donor site. Consequently, the only parameter bound to phonons, and experimentally acceptable, is the mean frequency v_{ph} (17) : $v_{ph}^2 = \frac{1}{3}(v_z^2 + v_y^2 + v_x^2) = \frac{1}{3} \cdot (v_z^2 + 2v_x^2)$, avec $v_x = v_y$. Let us call $\eta = v_z^2 / v_x^2$, which allows to establish a measurement of the anisotropy. It is equal to 1 for an isotropic structure which, in our model, represents the amorphous state, and it takes very high values for a very anisotropic structure, i.e. an ordered structure ($1 \leq \eta \leq \infty$). The expression of v_{ph} gives :

$v_z = v_{ph} \left(\frac{1}{3}(1+2\eta)\right)^{1/2}$. Calling $d = \left(\frac{1}{3}(1+2\eta)\right)^{-1/2}$ one obtains $v_z = d v_{ph}$. The quantity d , is equal to 1 when $\eta = 1$, that is when the structure is totally disordered and tends to 0 when the system is ordered. Thus this parameter can be related to an anisotropy parameter (10). In fact, the latter must be equal to zero for the most symmetric phase and different from zero in the least symmetric phase. With $p = 1 - d^2$, we

define an anisotropy parameter that meets this criterion capable to describe a transition due to the appearance of an ordered structure in an amorphous material :

$$p = (v_x^2 - v_z^2) \left\{ v_x^2 \left(1 + (v_z^2/2v_x^2) \right) \right\}^{-1} \text{ with } v_x \geq v_z \quad (4)$$

Taking into account $v_z = dv_{ph}$, the equation (2) leads to an equation containing d :

$$\sigma'(\omega) = \pi N_A N_D (72kT)^{-1} (2\alpha)^{-5} e^2 (\epsilon_z/\epsilon_x)^2 \{1 + 2(\epsilon_z/\epsilon_x)^2\} \omega (\ln(dv_{ph}/\omega))^4$$

Case 1. Isotropic : $\eta = 1$ or $d = 1$.

The solid corresponds to a totally disordered material, i.e. amorphous material. Using the approximation suggested by MOTT (4,5), $N_A = N_D = kTN(E_F)$, we find an expression identical (if we except the constant value) to the equation generally proposed for amorphous compounds :

$$\sigma'(\omega) = (\pi/3)kT(N(E_F))^2 \alpha^{-5} e^2 \omega (\ln(v_{ph}/\omega))^4$$

Under these conditions it has been shown (14) that the real part of the conductivity $\sigma'(\omega)$ varies as ω^s , that is :

$$\omega (\ln(dv_{ph}/\omega))^4 = C\omega^s,$$

where C is a constant. Studying this function leads to a value of s of the form (4) :

$$s = 1 - 4/\ln(dv_{ph}/\omega) \quad (5)$$

One can see that in the case where dv_{ph}/ω is large (with $d = 1$), which is always experimentally verified, $s \rightarrow 1$.

Case 2. η large, d small.

For a given phonon mean frequency v_{ph} , if d decreases, dv_{ph}/ω is such that according to equation (5), $s \rightarrow 0$. The conductivity becomes independent of the frequency. Between these two limiting cases, s is a decreasing uniform monotonous function of d in the interval $[0, 1]$.

II - Experimental verification. We have used the frequency dependent conductivity of "low temperature carbons" around a non-metal-metal transition (2). In fig.1 we have drawn the conductivity as a function of frequency (logarithmic scale, $T = 186$ K) for 3 carbons of heat treatment temperature (HTT) 600, 650 and 730°C. The values of s are 0.77, 0.61 and 0, respectively (2). We observe that $s \rightarrow 0$ when HTT increases. These carbons are gradually organized when HTT increases, i.e. the dimension of perfectly organized crystallites increases regularly (18). This result can be considered as a rather satisfactory experimental picture of the behaviour foreseen by the model proposed.

Fig.1 - Frequency dependence of the conductivity of 3 carbons ($T=186$ K) with increasing HTT.

Fig.2 - Simulated frequency dependent conductivity as a function of the anisotropy factor FA .

Fig.3 - Effect of the anisotropy factor FA , on the exponent s .

III - Calculation of the conductivity in an anisotropic model. To simulate numerically the proposed model we used a method of percolation. The lattice used here is derived from previous works (19,20) and is a square two dimensional 30×30 node lattice. Each node is bound to its neighbours by orthogonal bounds. The bound is considered as a good or a poor conductor according to the value of r : if r is greater than a

given threshold r_0 formally defined, the bound is considered as a good conductor and is then represented by a resistor R_0 . If not, it is considered as a poor conductor and represented by a resistor R_1 and a capacitor C_1 in parallel. In this work, the ratio R_1/R_0 is taken equal to 104. We have simulated the anisotropy of the material by introducing an anisotropic factor FA, as follows : every bound of the lattice is scanned one after the other. Each time we meet a conducting bound B, it is extended by FA-1 conducting bounds along the direction perpendicular to the electrodes, independently of the previous values of these bounds. Thus we introduce into the lattice sequences of FA-conducting bounds along the direction perpendicular to the electrodes. Obviously FA depends on the extent of organization of the lattice, so that FA = 1 represents an isotropic structure. We obtain a new complex correlated lattice in which the potential is calculated at each mode by the Gauss-Seidel iteration procedure improved by a relaxation process described elsewhere (21). In order to reduce the computation time, the rate of conducting bounds is set to 15.3 %. Then the conductivity σ of the simulated material is known for a given voltage and frequency. Drawing $\log \sigma$ as a function of $\log \omega$ for various values of the anisotropic factor, we obtain the results shown in fig.2. We observe a noteworthy likeness between the family of experimental curves (fig.1) and the curves obtained by simulation (fig.2). Moreover we find the experimental evolution of s (fig.3). The high values found for s , in an isotropic solid can be explained by the simplicity of the two-dimensional model designed to interpret the behaviour of a three-dimensional solid.

III - Conclusion. Considering the equation (5), we find :

$$s = 1 - 4/\ln \left(\frac{v_{ph}^{(1-p)1/2}}{\omega} \right)$$

where p is the anisotropy parameter formally defined (equation 4). The proposed model leads to a relation that binds explicitly the s exponent to a structural parameter p , on a large range of frequencies. p characterizes some insulator-semiconductor transitions associated to the gradual appearance of an order in initially amorphous solids. The s parameter, that can be directly obtained experimentally is a convenient way to evaluate the order in some cases.

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