

# Hopping conductivity with a diffusion of neutral trapping centers

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A new conductivity mechanism in high-resistivity materials is analyzed: a charge transport as a result of hops of carriers among neutral trapping centers which are themselves diffusing. It is shown that this mechanism can explain the anomalous photoelectric phenomena which are observed in ruby crystals.

1. An unusual phenomenon has recently been discovered and studied in ruby crystals<sup>1</sup>: the formation of electrical domains with a field  $\sim 10^6$  V/cm. This effect has been explained<sup>2</sup> on the basis of a current flow opposite the field upon exposure to light: an absolute negative conductivity. It has been established<sup>3,4</sup> that this photocurrent is caused by the excitation of neutral impurity centers of chromium in a metastable  ${}^2E$  state (ruby has essentially no dark conductivity).

The large body of experimental evidence indicates that the photoconductivity of ruby stems from hops of charge carriers among centers which have been excited to a  ${}^2E$  state.<sup>3,4</sup> In particular, this picture explains the observed change in the sign of the current as the frequency of the resonant excitation is scanned within the  $R$  line ( ${}^4A_2 \rightarrow {}^2E$ ): Depending on the frequency, neutral centers to the right or left of the charge carrier (if the field is directed from left to right) will be excited predominantly, and this effect will determine the direction of the hop. This spatial selectivity of the excitation stems from the difference between the shifts of the  $R$  lines of these centers under the resultant influence of the applied field and the Coulomb field of the charge carrier. A theory of a hopping photoconductivity in ruby based on the ideas of Refs. 3 and 4 was derived by Novikov and Sturman.<sup>5</sup>

At the same time, the suggestion of a hopping conductivity in ruby sharply contradicts the experimental dependence of the photocurrent on the chromium concentration  $N$ . This dependence is approximately linear as the average distance between impurities,  $R = N^{-1/3}$ , varies over the interval<sup>6</sup> 15–40 Å. The theory of hopping conductivity<sup>7</sup> predicts an exponential dependence  $\sim \exp(-1.73R/a)$ , where  $a$  is the trapping radius. At the value  $a \approx 1$  Å, characteristic of the chromium ion, the exponential factor changes by 18 orders of magnitude in this interval, while the experimental photocurrent changes by a factor of 15. In order to reconcile theory and experiment we would have to assume  $a \approx 16$  Å, but this value seems totally improbable.

2. In the present letter we wish to propose a new charge-transfer mechanism, specifically, a diffusion-hopping mechanism. We show that the contradiction we just noted can be resolved if the photoconductivity of ruby is caused by this mechanism. Let us assume that the neutral centers, along which the hopping occurs, are capable of

moving through the crystal by virtue of a photostimulated diffusion. A neutral center can approach a charged center to within a small distance, causing an exponential increase in the probability for a hopping of a charge carrier (we are assuming that the charged centers do not diffuse).

As we will show, this mechanism leads to a linear, rather than exponential, concentration dependence for the photoconductivity, in agreement with observations. The absence of a dark conductivity can also be explained in a natural way. In the ordinary theory of a hopping conductivity this fact can be explained only by assuming that the localization radius in the ground state is substantially smaller (by a factor of about three) than in the excited state. This situation would be unlikely since the electronic configurations of chromium in the  $^4A_2$  and  $^2E$  states are identical.

The other experimental results can be explained in this new model by analogy with the arguments of Refs. 3 and 4. For example, the sign of the resonant photocurrent is determined by the circumstance that the spatial selectivity of the excitation will cause a predominant diffusion of either the right-hand or left-hand neighbors of the charge carrier, depending on the frequency. A neutral center will then approach a charged center predominantly from one side, and this effect will determine the direction of the hops.

To the best of our knowledge, there has been no study of photostimulated diffusion in ruby, but its occurrence in other crystals has been firmly established. One mechanism for this diffusion involves a transition of impurity atoms to an excited state<sup>8</sup>; we are suggesting that this mechanism also applies to chromium in ruby.

One consequence of this new model is the following: A photostimulated diffusion of chromium should lead to a burning of holes in the nonuniformly broadened  $R$  line. Specifically, chromium atoms excited by a narrow line should diffuse until they escape from resonance as a result of a change in the local value of the random field. After the illumination is ended, the holes should remain. Similar holes were observed in Ref. 4 but not studied in detail.

3. The mechanism which we are proposing here for an increase in the hopping conductivity, through a diffusion of neutral trapping centers, may operate in insulators and compensated semiconductors if the charge transport occurs among deep centers. The diffusion may be either photostimulated (as we are suggesting in the case of ruby) or thermal. The competing band conductivity mechanism is unimportant if the diffusion activation energy is lower than the ionization energy of the impurity.

Let us estimate the charge-carrier mobility associated with this diffusion-hopping transport mechanism. The typical hopping length  $r$  is found from the condition

$$r^2/D = \tau_0 \exp(2r/a). \quad (1)$$

The left side here is the time taken by a neutral center to diffuse a distance  $r$  ( $D$  is the diffusion coefficient), while the right side is the time required for a hop over a distance  $r$ . Assuming  $D \ll a^2/\tau_0$ , we find  $r = (a/2) \ln(a^2/D\tau_0)$  from (1).

The time which elapses between hops,  $\tau$ , is equal to the average time over which a neutral center comes within a distance  $r$  of a charged center. The hopping frequency is therefore determined by the diffusive flux to a sphere of radius  $r$ :

$$\tau^{-1} = 4\pi DNr, \quad (2)$$

where  $N$  is the concentration of neutral centers. The diffusion coefficient of the charge carriers is obviously  $D^* \sim r^2/\tau$ . We thus have

$$D^* \sim DNa^3 \ln^3(a^2/D\tau_0). \quad (3)$$

The condition for the applicability of (3) is  $a < r < R = N^{-1/3}$  (at  $r > R$ , this mechanism is less effective than the ordinary hopping conductivity).

If the elementary event—the hop of a charge carrier—does not involve optical excitation, the mobility is related to  $D^*$  by Einstein's relation. The mobility turns out to be proportional to the concentration of neutral centers. In the case of a photostimulated diffusion, the mobility is also proportional to the light intensity.

In ruby, because of the spatial selectivity of the excitation which we discussed above, the coefficient of photostimulated diffusion,  $D$ , will depend on the local electric field, so Einstein's relation will not hold. We can estimate the current density  $j$  by assuming that as a result of the selectivity, the diffusion of neutral centers from one side of a charge carrier is significantly faster than that from the other side. We can then write

$$j \sim enr/\tau \sim enNDa^2 \ln^2(a^2/D\tau_0), \quad (4)$$

where  $e$  is the charge of an electron, and  $n$  is the concentration of charged centers ( $n \ll N$ ). We do not know the value of  $n$  for ruby. Adopting  $n = 10^{-2} N \sim 10^{18} \text{ cm}^{-3}$ , we find that the experimental value ( $j \sim 10^{-9} \text{ A/cm}^2$ ) is reached at  $D \sim 10^{-15} \text{ cm}^2/\text{s}$ .

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