HOPPING CONDUCTIVITY IN (Zn,Fe)Se INTENTIONALLY DOPED WITH Ag

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The transport phenomena in (Zn,Fe)Se were studied. In order to obtain iron centers in Fe^{3+} charge state the crystals were doped by Ag what produces acceptors compensating Fe^{2+} donors. The results are explained in terms of thermally activated jumping of charges between Fe^{3+} and Fe^{2+} centers. The nature of activation energy is discussed. The polaron model seems to be not valid in our case. The Coulomb interaction between charged acceptors and "holes" on iron centers is considered as the origin of thermal activation of jumps. We suggest the deviation from random and mutually independent distributions of charged Ag acceptors and Fe^{3+} ions resulting from the electrostatic interactions between them at high temperatures.
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More than 20 years ago studies on transport phenomena in phosphate glasses containing transition metal (TM) ions were carried out [1, 2, 3]. The thermally activated hopping of charges between TM ions in various charge states was proposed as the mechanism of conductivity.

One may expect that a similar type of hopping could be observed in the II–VI semimagnetic semiconductors in which the levels of TM ions lie deep in the energy gap. We investigated the transport phenomena in the (Cd,Fe)Se crystals, where the $Fe^{2+/3+}$ donor level lies about 600 meV above the top of the valence band. The results were interpreted in terms of "holes" (Fe in Fe^{3+} charge state) jumping to the nearest Fe^{2+} centers [4]. A certain number of Fe^{3+} ions is believed to result from the compensation caused by unidentified acceptors present in the crystals.

Now we report the results of the studies of transport phenomena in (Zn,Fe)Se mixed crystals. In this material the $Fe^{2+/3+}$ donor level lies about 700 meV above the top of the valence band [5, 6]. The as-grown crystals with iron content $0.6 \div 5$ at.% are semiinsulating. Their conductivity at 293 K is lower than 10^{-10} S/cm. To produce Fe^{3+} centers necessary for hopping conductivity one has to dope the crystals with acceptors compensating iron donors. The Ag was chosen
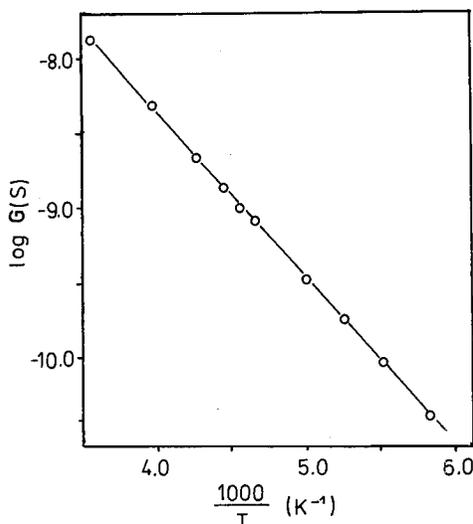
Fig. 1. The temperature dependence of conductivity. The slope of the line corresponds to 230 meV.

as a dopant because of proper position of its level (430 meV above the valence band) and its effective diffusion. The diffusion of Ag during 10 hours at 800 K caused significant increase in the conductivity up to about 10^{-7} S/cm. The temperature dependence of conductivity is shown in Fig. 1. The slope of the line corresponds to the activation energy $\varepsilon = 230$ meV. The observed sign of the thermopower indicated the hole type of conductivity. In our case $[Fe^{3+}] \ll [Fe^{2+}]$, which means that the Fermi level is pinned to the $Fe^{2+/3+}$ level. If the observed p-type conductivity were due to band holes — 700 meV would be expected as the value of ε. The obtained value 230 meV is quite absurd in the band picture.

The Hall voltage at 293 K turned out to be unmeasurably small and the estimated upper limit of Hall mobility was 0.1 $cm^2/(V\ s)$. In the case of band conductivity the Hall voltage turns zero when $p/n = \mu_e^2/\mu_h^2$. On the other hand the product $p \times n$ is determined by the known values of μ_n, μ_p, N_c, N_v and E_g for ZnSe. Thus, assuming the band transport, the value of conductivity at a given temperature can be calculated. For 293 K we get $\sigma = 2.4 \times 10^{-15}$ S/cm. This value is in a drastic disagreement with the value 1.2×10^{-7} S/cm obtained from the experiment. Thus, the band transport cannot be responsible for the observed conductivity. The assumption of a non-band transport, namely the hopping of charges between iron centers, allows us to explain all the presented results in a consistent way.

Now we are going to consider the origin of the activation energy. The hopping of polarons was often suggested in the papers on transport phenomena in glasses containing TM ions. The activation energy was believed to result from the local lattice deformation around the charged center. For (Zn,Fe)Se this model does not

seem to be valid. The lattice relaxation energy related to iron centers in ZnSe:Fe was (rather carefully) estimated to be below 100 meV [5, 6]. Even smaller value 20 meV was determined for CdTe:Fe [7].

These results lead to the conclusion that the observed activation energy of the hopping conductivity is significantly higher than the lattice relaxation energy related to iron centers. Thus another model ought to be taken into account. Mott et al. [8], Miller and Abrahams [9], Shklowskii and Efros [10] and others analysing the hopping conductivity in compensated semiconductors have ascribed the activation energy ε to the Coulomb interaction. It is the energy required to remove a "hole" on donor site from the nearest negatively charged acceptor, i.e. $\varepsilon = e^2/(\kappa R_{\mathrm{AD}})$, where κ is the dielectric constant, R_{AD} — the average acceptor–donor separation. The authors assumed $N_{\mathrm{A}} \ll N_{\mathrm{D}}$, random and mutually independent distribution of impurities, and got:

$$\varepsilon = \frac{e^2}{\kappa R_{\mathrm{ASD}}} = \frac{e^2}{\kappa} \left[\frac{4}{3} \pi N_{\mathrm{D}} \right]^{1/3} , \tag{1}$$

where R_{D} is the average donor–donor separation. Using this formula and taking $N_{\mathrm{D}} = 2.2 \times 10^{20}$ cm^{-3} (1 at.% of Fe) we get $\varepsilon = 140$ meV. It is rather close to the experimentally found values. But we did not find in the experiment the implied by the formula (1) relation between ε and N_{D}. In order to test this relation, two samples of iron content 0.6 and 5 at.% were treated in common: covered with Ag, annealed and quenched. The expected ratio between the values of ε for both samples was about 2.2. The found values of ε turned out to be practically equal. One may suggest that the assumption of mutually independent distributions of acceptors and donors is not true in our case. In contrary to the situation considered by Mott and others we are dealing with high concentration of donors having well localized wave functions. The Coulomb interaction between charged Ag acceptors and Fe^{3+} ions has not to be neglected. It may cause shortening of distances between them at high temperatures during technological processes. Thus, after quenching of crystals, the "frozen in" distribution would differ from the assumed random and mutually independent one. It may lead to a little higher values of ε.

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