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To The Theory of Inverse Transition Insulator-Metal Anion Defective Ferromagnetic Semiconductor $Euo_{1-\delta}$

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Abstract. Based on the available experimental data are made model estimates and the implementation criteria of inverse electron transition insulator-metal set in the "classical" ferromagnetic semiconductor - europium monoxide which is the base model of research in semiconductor spintronics.

Keywords: Ferromagnetic semiconductor, europium monoxide, insulator-metal transition, non-stoichiometry, local electronic level, magnetic polaron

In connection with the continued works in recent years the rapid development in the physical materials field of semiconductor spin electronics (spintronics) as a model of research has been and remains a "classic" ferromagnetic semiconductor - europium monoxide - EuO [1]. A characteristic feature of its crystal chemistry is that it is a phase of variable composition, $EuO_{1+\delta}$, which extends the boundaries of homogeneity in the area of excess ($\delta<0$), and the lack of ($\delta>0$) metal. True nonstehiometric area it is fairly narrow: δ -index varies between $0> \delta> 0.005$ (excess metal) and $0 <\delta <0.035$ (excess oxygen). [2] However, depending on the oxygen content significantly are changing the properties monoxide, in particular, the electrical conductivity. At the same time regardless of the sign δ it is always characterized by n-type and its temperature dependence is typical for semiconductors. The specific conductivity values of EuO phase at room temperature are in the range $\sigma = 10^{-8}$ — 10^{-12} $(\text{Ohm}\cdot\text{cm})^{-1}$. In the case of excess metal (i.e. anionic defects) samples $EuO_{1-\delta}$ - phase below the Curie temperature (T_c = 69.4 K) at the $T_i \approx$ 52 K to test the temperature insulator-metal transition (I - M) with a conductivity jump 13 — 15 orders of magnitude [3,4] (Fig.1). A greater jump in the specific electrical resistivity of conductive solid phase is observed only in the superconducting transition in them. In this case, for the phase $EuO_{1-\delta}$ it is the second largest known today jump electrical conductivity in crystals. Moreover, it is the first of the public when it *becomes metal the low-temperature ferromagnetic-ordered phase.* To date, similar to the character of semiconductor-metal transition, although with a much smaller jump of electric resistivity, $\Delta\rho/\rho$, is known for some compounds doped of the ferromagnetic ordered lanthanum manganites – the magnetic semiconductors, a value of T_c which is capable of more than room temperature [5]. Since the physical nature the I – M- transition in this class of materials has a lot of similarities, we reproduce here the most adopted model previously proposed for europium monoxide and, as we see, there is no other alternative. Illustration of this transition for $EuO_{1-\delta}$ crystals with an index of $0 <\delta<0{,}005$ in Fig. 1 also reproduces the effects of an external magnetic field [6].

It is evident that the latter shifts the temperature of the electronic transition in the direction of its increase, several reducing the magnitude of the jump $\Delta\rho/\rho$, but without destroying the character of the transition. It should be noted that the insulator-metal transition in a defective oxygen europium monoxide phase is merely cooperative nature and occurs only for a narrow range of concentration of charge carriers therein, $n = (1 — 2) \cdot 10^{19}$ cm^{-3}. Already at values $n \geqslant 3 \cdot 10^{19}$ cm^{-3} called transition in crystals $EuO_{1-\delta}$ not observed and the monoxide becomes a quasi-metal for the entire temperature range.

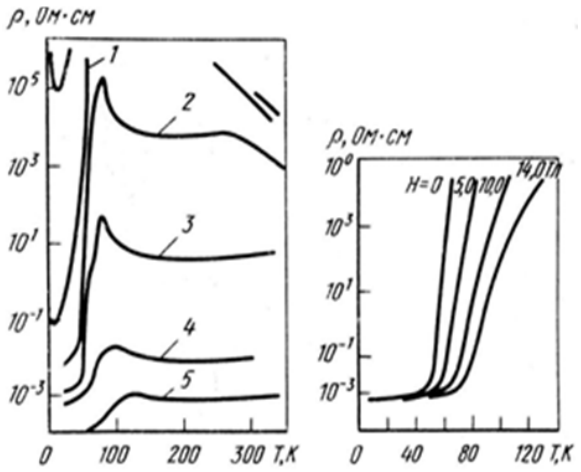

Figure 1. Transition insulator-metal samples $EuO_{1-\delta}$ at T_i = 52 K in the absence and with the presence of an external magnetic field. Curves 1 - 3 describe compositions $0<\delta<0{,}005$; Curves 4, 5 refer to solid solutions $Eu_{1-x}Gd_xO$ with x = 0.01 (4) and x = 0.02 (5), respectively.

The mobility of charge carriers in the europium monoxide is sufficiently small in comparison with nonmagnetic semiconductors $A^{III}B^{V}$. At room temperature, it is the value of u = (10 — 30) $cm^2/(V \cdot s)$. With decreasing temperature, the mobility of carriers in crystals EuO increases almost an order of magnitude, and at T = 4,2 K, it reaches the value of $u = (2 — 4) \cdot 10^2$ $cm^2/(V \cdot s)$. Its monoxide in the magnetic phase transition area (Curie temperature, MPT) is peculiar and large negative magnetoresistance effect, $(p_o - \rho_H)/p_o$, reaching around the value of 10^6 for the crystals with the non-degenerate electric conductivity [7].

Another characteristic feature of the electrical (and optical) properties of these crystals is the presence of large effect "Red" bias own optical absorption edge (the bottom of the empty conduction band, ΔE_g) at magnetic ordering. At T = 20 K ΔE_g shift EuO reaches value ΔE_g = 0.25 eV. In an external magnetic field in terms of increasing crystal magnetization this shift increases by almost 10% [7]. From the known to date, the list of magnetic semiconductors match the magnitude of the red shift of the optical absorption edge with the above data can, again, only the crystalline phase based on manganese lanthanide in which ΔE_g value can reach to different levels of doping with 0.16 to 0.2 eV [8, 9].

EuO is a ferromagnetic semiconductor with a predominant of the itinerant conduction mechanism. This is also indicated for the characteristic temperature behavior of it electric resistivity at the paramagnetic ($T > T_c$) region where it varies according to the relation

$$\rho(T) = \rho_o exp(\Delta E / kT) \quad (1)$$

in which the activation energy of conduction is ΔE = 0,6 — 0,8 eV. The appearance of a spin's order in it for temperatures $T<T_c$ is reflected in the form of (1) which becomes dependent on the reduced spontaneous magnetization of crystals, M:

$$\rho\left(T\right) \sim \text{const}\left[1 + M^2\left(T\right)\right] \quad (2)$$

Also indicative features of critical behavior $EuO_{1-\delta}$ samples in the temperature range of the magnetic disordering. Therefore, it is quite natural to identify the nature of electronic insulator-metal transition with the presence at the defect structure of the crystal O - vacancies [10]. At low concentrations, they form isolated between yourself a doubly donor levels (vacancies) in the electronic band spectrum of the crystal [11]. In the context of the local environment of magnetically active cations Eu^{2+} (z_1 = 6) the oxygen O^{2-} -vacancy is a polaron with a small radius, because the interaction energy of the local levels electrons with the *4f* - spins cations europium limits distances of the order (4 — 5)a (a - lattice parameter). Therefore, the existing models and I–M- transition in EuO used notions of magnetic (spin) polaron associated with O-vacancies [12, 13]. Otherwise, such an electronic state of oxygen vacancies in the europium monoxide has been called "related" magnetic polaron [14]. In contrast to these electronic states of O-vacancies in the monograph [15] used the concept of "free" magnetic polaron introduced in

Kasuya and Yanaze consideration in connection with the doping of the data in the system (EuO + Gd). The differences in concepts relating to the two sides of the problem: first, free polaron there (shows itself) in a limited temperature range near T_c, while the related magnetic polaron is stable in a rather wide range of temperatures, in principle, from 0 K to T_c. Secondly, magnetopolaron bound states suggest the existence of "deep" ($\Delta E \approx 0.3$ eV) electron donor levels relative to the top of the conduction band of the crystal. Doping also considers the presence of "small" donor levels (impurity or magnetic state) with an order of magnitude less energy. Let us consider in more details the physical model of I – M-transition at EuO.

At the ferromagnetic ordering crystal with metallic conductivity is dominated by the exchange interaction between the spins of the conduction electrons and the magnetic moments of the lattice sites (J_{eff}). The minimum total energy of the system at T = 0 K, is achieved in the case of both parallel spins. At T > 0 the spins of the lattice nodes under the influence of the thermal phonons begin disordered. The spins of the conduction electrons thus exhibit a tendency to polarize them, restoring, to some extent, a certain degree of ferromagnetic order in the crystal. In the case of low concentration of charge carriers in the crystal (quasimetal or degenerate semiconductor) is possible and energetically favorable emergence in it of spatial regions with high (compared with the average over the crystal) ferromagnetic order. Such areas are able to move through the crystal like a polaron with certain activation energy (E_p), which characterizes the width of a polaron band (W_p). The latter is associated with the temperature of the relation [12]:

$$W_p = J_{eff} exp(-y) \tag{3}$$

where y=| E_p |/ω(ω-cyclotron frequency of carriers).

Increasing the temperature of the crystal leads to a strong narrowing of a polaron band, and if the value W_p is less energy bottom of the conduction band, then there is a gap between them. What has been said so far defines common features I - M- transition. A feature of the rare-earth semiconductors is that they manifest a clear dependence of the conduction band width of *s*- or *d*- orbital nature of electrons interacting with unfilled shells *4f*- cationic lattice sites. The europium monoxide is significant also the magnetic exchange between them, leading to a decrease of the conduction band bottom - for its "red" shift at T < T_c. The foregoing is the reason that EuO at certain degree of conductivity degeneration, namely, when the carrier concentration therein: $n^* \approx (1 — 2) \cdot 10^{19}$ cm^{-3} and T < T_c bottom of the conduction band, dipping, intersects with the polaron levels of vacancies — the system becomes conducting (metal) state (Fig. 2). Estimates show that at the red shift $\Delta E_g \approx 0.25$ eV and width $W_p = \Delta E \approx 0.3$ eV in view of the dependence (3) temperature I - M - transition corresponds to T <100 K.

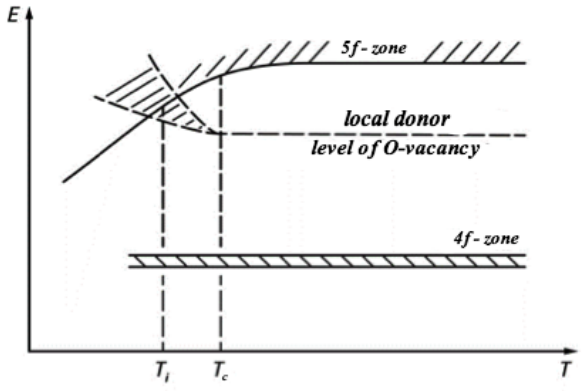

Figure 2. Electronic circuit insulator – metal transition in $EuO_{1-\delta}$ (H = 0) at the temperature $T_i < T_c$.

Thus, to understand the nature of I – M- transition in $EuO_{1-\delta}$ we need to know the status and value of the exchange of electronic levels of O^{2-}-vacancies with the nearest magnetic neighbors. Since these vacancies are the doubly charged, the electrons in them can be in the states $1s^2$ or *1s2s*. In the first case considered so-called *He* - shaped models of I-M-transfer, in the second - the *H*-shaped model - bound

magnetic polaron model. It is clear that these models differ in the definition of the ground state of the electrons O^{2-}-vacancy. Moreover, these differences are most significant for the paramagnetic region monoxide. Indeed, at *He*-like model two electrons of oxygen vacancies have spins directed singlet with respect to each other, while all spins of the cationic units Eu^{2+} at $T>T_c$ already disordered and paramagnetic susceptibility of the crystal will not contain additional contribution $\Delta\chi_m$ observed, however, experimentally. The second model assumes a triplet spin state of electrons O- vacancy at the same temperatures. It is their condition capable of causing local polarization already disordered spin $4f^7$ electrons of europium to form domains (or clusters) that retain the short-range magnetic order. Consequently, the latest model better matches the observed magnetic and thermodynamic experimental data [16]. With the localization of O-vacancy electrons form an associated magnetic polaron within which the degree of ordering of the spin and the magnetic energy stored in a fairly wide temperature range for $T > T_c$.

In the state of ferromagnetic ordering monoxide at $T < T_c$ differences between these two models, at first glance, are virtually absent. Due to the splitting of the electron orbital levels of O-vacancy caused by magnetic energy, they are delocalized and their true position in the band gap determined by spontaneously increasing while the magnetization of the crystal and a "red" shift of the bottom of the conduction band. Consequently, the two discussed the model can explain I - M-transition in $EuO_{1-\delta}$. At the same time, magnetic and thermodynamic behavior of the monoxide in $T > T_c$ [16], it is better described by the *H*-like model - a model bound magnetic polaron.

Attempting a qualitative generalization both of these models based on only the electrical characteristics of the defective oxygen monoxide was made in [17]. Tolerance of impurity levels varying electron concentration associated with an excess of europium at the metal phase (EuO + Eu). With that energy's depth of their occurrence in the zone constantly increases with increasing concentration of n^*, so that at a certain excess metal system acquires metallic conductivity.

Attempts were also made purely theoretical consideration of the problem of insulator-metal- transition in EuO. For example, in [18] in the linear approximation calculated properties of the electron gas the spin's order of carriers in which is required as an exchange between the localized moments of the cations and the Coulomb interaction of donors. Mott instability of the exchange-polarized electron gas that is responsible for this transition is calculated. In the article [19], the authors attempt to calculate the electron gas exchange polarization function that is regarded as a perturbation of the concentration of charge carriers. The resulting solution of the corresponding equations linearized perturbation theory is valid only in the spin-wave region. However, the authors were able to establish a co-operative nature of the phenomenon, showing the dependence of I–M -transition of the electron concentration - donors. This result is in good agreement with experiment, but also does not favor any of the above applications of its models.

Finally, in [20] identified the electrical and magnetic properties of the electron gas in a lattice of local spins, ferromagnetic ordering which are obliged to *s* - *f*- exchange interaction. It was carried out the separation of electron charge and spin density of localized moments, taking into account the received initial perturbation of the electron gas - or only the electric or only magnetic. However, an unambiguous conclusion about the nature I – M- transition could not be obtained: perhaps this is due to the one-electron donors to review the system, forming an impurity band at a certain critical concentration. Such an approach to the phase $EuO_{1-\delta}$ is not entirely correct, because the oxygen vacancies monoxide is a divalent electron donor. This fact was taken into account by the authors [21], proposed a mechanism insulator-metal transition by changing the ground state of doubly charged donor when you change the local magnetization of the crystal. Shown, when at $T = 0$ K *1s2s* ground state energy of the donor is lower than the state $1s^2$ and the system is a metal, then at a certain temperature T_i inversion possible terms and donors will be able to $1s^2$-system becomes an insulator. In this case, collectivization of electrons at the temperature $T < T_i$ occurs only at a certain concentration n^* and subject to the feasibility of the Mott criterion: $n^{1/3}r > C$, where r - the radius of the hydrogen electron orbit, defined as $r = \pi^2\varepsilon/m^*e^2$. Where $C = 0.6$, and ε - dielectric constant of the material. The paper concludes that the transition I - M is possible when the inequality: $n^{1/3}\, r_2 > C > n^{1/3}\, r_1$ (r_1 and r_2 is radii orbits of *1s*- and *2s*-electrons) is performed. Then, at high temperatures ($T > T_c$) system is an insulator, and when the inversion temperature, it becomes conductivity characteristic of metals. From this it follows that for carrying out of the specified transition the Mott criterion will be performed for *2s*- electron state (delocalization) and not be satisfied in the case of *1s*- state (localization). Otherwise, the system would

be an electrical conductor ($n^{1/3}\ r_1 >$ C), or insulator ($n^{1/3}\ r_2 <$ C) at all temperatures. However, in the region T < T_i results [21] do not establish certainty between *He*- and *H*- similar models of I - M-transition in EuO.

If at T = 0 K preference the second model, the transition in the donor T > T_i in *He*-like state, as mentioned above, contrary to the available experimental data. It can be stated that based on experimental results, apparently, it is difficult to give preference to any of the theoretical models I–M-transition in ferromagnetic ordered state (T<T_c) of $EuO_{1-\delta}$ phase. However, for the paramagnetic (T> T_c) the state of the matrix observed properties monoxide $EuO_{1-\delta}$ in better agreement with the model bound magnetic polaron (*H*-model Torrance et al. [22]). Therefore, it can be assumed that this model is preferred to characterize this transition. This conclusion does not contradict the results of [23], where an anomalous behavior of the conductivity activation energy factor of pressure for EuO compositions possesses I - M-transition: β = kT (d lnρ/dP). As it turned out, for them the value of $\beta > 4{,}4 \cdot 10^{-11}$ eV/Pa, i.e. exceeds the previously set Wachter [24] for monoxide and position of Oliver et al. [4] on the basis of consideration of a *He*-like model of such transition.

Experiments using high pressure lead to a linear reduction in Lnρ, while the electrical resistivity of the samples are satisfied of dependent: $\rho(P) = \rho_0\ exp\ \{\beta P/kT\}$, and its rising at the room temperature accompanied by a decreasing in the value of β. The author of [18] considered the totality of the data in favor of the transition on Torrance model [22].

If you go back to the conclusions [16] on the impact of O- vacancies on the critical exponents of the MPT-2 crystals $EuO_{1-\delta}$-phase, it is possible to conclude that observed in this case near T_c contribution to the magnetic dipole-dipole interaction in their values, leading to the need for renormalization of the latter will also be explained by the existence in $EuO_{1-\delta}$ magnetopolaron states associated with O-vacancies.

Thus, summarizing the above, we can draw the following conclusions: O^{2-}- vacancy in the ferromagnetic-ordered matrix $EuO_{1-\delta}$ is a doubly charged donor, forming a deep local magnetopolaron energy levels respect to the bottom of the conduction band. This is the difference from the one-electron impurity states in doped and non-degenerate magnetic semiconductors, energy depth of which is significantly less. The fact that the I – M- transition in the $EuO_{1-\delta}$-phase observed in a relatively narrow concentration range of existence of O vacancies (0<δ<0,005), apparently, is not accidental. In larger their concentrations (δ > 0,005) system(EuO+Eu) becomes "Metal" with dependence on the carrier concentration increased Curie temperature. That, in turn, indicates the degeneration of local polaron levels O-vacancy into the appropriate impurity band, combined with *5d - 6s* - conduction band europium ions. That a polaron level of O-vacancy at EuO remain energy localized surrounded by six Eu^{2+} ions nearest neighbors, itself single O-vacancy will be account for no less than three elementary cells monoxide, i.e. defend one another at distances of the order of $r_0 \approx 3a\sqrt{2}$. In this case, if we take into account, the total number of cationic and anionic components such expanded cells (N = 72), we can determine the maximum possible concentration of isolated O^{2-}-vacancies are appropriate of the nondegenerate conductivity $EuO_{1-\delta}$ as: $1 \cdot 100\%/3N = 0{,}47\%$. Accordingly, the ultimate composition of the oxygen non-stoichiometry of $EuO_{1-\delta}$ will be: $\delta = 0{,}0047$, that is true.

In larger concentrations O-vacancy will be located from one another already at shorter distances, so that there will be "related" vacancy. In such cases, one can speak of the degeneration of the semiconductor conduction deficient anion monoxide, because of its electron spectrum near the bottom of the conduction band occurs zone of the polaron local levels. Due to the effect of "red" shift the latter will merge with *5d - 6s* - conduction band, leading to a sharp increase in the concentration of charge carriers and increase super exchange between *4f*-spins of europium cations, and increase T_c of (EuO + Eu) system. This process, in turn, is accompanied by a reduction in the unit cell volume of the crystal, in which he is similar to the action of hydrostatic compression EuO crystal under conditions imposed on it by the high pressure and changing the parameters of the band gap in the electronic spectrum, $dE_g/da > 0$ [25].

A theoretical estimate of the maximum concentration of the electron density (in the one-electron approximation), corresponding to the case isolated magnetopolaron levels of O-vacancies in $EuO_{1-\delta}$ electronic spectrum, gives a value of $n_o \approx 2\ N_L\ /\ 3 = 1.8 \times 10^{19}$ cm^{-3} (the N_L-Loschmidt number) . A further increase in the concentration of charge carriers to the $n^* > n_o$ case will correspond to the appearance of "related" O-vacancies and transition phase $EuO_{1-\delta}$ at the state with metallic conductivity character for the entire temperature range. Moreover, using the assessment made can be established that

in the case of isolated (non-interacting) O-vacancies, when the radius of the electron correlation $r_o < a$, Mott criterion for implementation I-M- transition $n^{1/3}\ r_o < 0.6$ is not satisfied, i.e. the system remains in a state of non-metallic. However, a slight increase n^* (already up to 3×10^{19} cm^{-3}) leads to reverse inequality and the feasibility of the Mott criterion for carrying out the electronic transition. In the case of a defective crystal $EuO_{1-\delta}$ it must comply with the temperature $T < T_c$ (i.e. $T = T_i$), in which with the growth of the spontaneous magnetization of the crystal occurs growth the values n^* and r_o. What is also consistent with the conclusions [21].

Under these conditions, the degree of destruction of long-range magnetic order in a crystal $EuO_{1-\delta}$ near the Curie temperature weakened due to different radii of critical fluctuations of the spins of the cations Eu^{2+} ($a = 2r$) and the spins of the electrons O- vacancies, because the ratio of $r\ /\ r_o$ <1. That may well be the cause of the observed degradation of MPT-2 of this crystal. The very same electron's I – M- transition in it at $T = T_i = 52$ K in accordance with the opinion of [21] it may well be a phase transition of the first kind (PT-1). In the experiment, however, in the temperature range 50 — 69 K anomalies on polytherms C_p (T) and M (T) for $EuO_{1-\delta}$ crystals are not observed, which may indicate either a strong localization of this inverse transition, or even cast doubt on its implementation as a PT-1.

In conclusion, we call attention to yet another convincing evidence of possible manifestations of magnetic polaron in $EuO_{1-\delta}$ and localization of charge carriers near the oxygen vacancies. They refer to the publications [26, 27] devoted to the study of the Electronic Paramagnetic Resonance (EPR) EuO samples of different composition. Thus, in crystals monoxide having I – M -transition, there was a significant decrease in the g-factor of the conduction electrons (about ≈ 3.5%) and increase in the numerical derivative $\mathrm{d}\Delta H_{\mathrm{EPR}}/\mathrm{d}T$ (more than 6 times) in comparison with similar values EuO crystals of stoichiometric composition (here ΔH_{EPR} - the width of the EPR line). These results clearly indicate that the electrical conductivity of the defective O-crystals made quasiparticles heavier than electrons. As a result of which there is practical no a mechanism of exchange narrowing of the EPR width line, which is due to the conduction electrons, as known [27].

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