New mechanism of transition of degenerate ferromagnetic semiconductors into the insulator state

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The transition of degenerate EuO from a conductor into an insulator is attributed to pairing of the electrons of the doubly-charged donor (oxygen vacancy).

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An unusually interesting phenomenon was observed in ferromagnetic EuO semiconductors with excess Eu. With increasing temperature, in a definite interval of the carrier density n, samples that behave at $T \to 0$ in the manner usual for degenerate semiconductors, go abruptly into an insulator state with a resistance higher by 13—15 orders of magnitude.[1,2] A theory that accounts correctly for the dependence of the effect on n was developed in[3–5] (see the review[6]). These papers dealt with a system of singly-charged donors with a concentration exceeding that limiting value, starting with which collectivization of the electrons of the donors takes place at $T = 0$, and the impurity band is produced. The energy of the electron is lower the higher the degree of the ferromagnetic ordering in the region where it is located with maximum probability. Therefore when the temperature is increased, each of the collectivized electrons exhibits a tendency to become localized on its own donor: the local magnetic order is destroyed more slowly than the long-range order.

Yet the oxygen vacancies, which determine the electric properties of EuO + Eu, are doubly-charged donors, and the theory of[3–5] can be generalized to include them only under certain conditions. The fact that the metal—insulator transition in EuO doped with a singly charged donor impurity Gd has not been observed in experiment[7] makes it necessary to investigate other mechanisms of such a transition, which are peculiar to doubly-charged donors. (The theories developed earlier in[8,9] on the basis of a model of a doubly-charged donor lead to independence of the effect of n, in contradiction to the experimental data.)

We propose below for the insulator—metal transition a mechanism connected with the change of the character of the ground state of the doubly charged donor with changing local magnetization. If we describe the donor by a helium-like model, then in a nonmagnetic crystal its ground state would always be $(1s)^2$ with the spins of the two electrons antiparallel. In a ferromagnetic crystal, however, the state $(1s)(2s)$ may turn out to be more favored, since the energy E_{12} consumed in the transfer of one of the electrons from the $(1s)$ to the $(2s)$ state can be offset by the energy of their exchange interaction with the magnetic atoms. If the spins of both electrons are parallel to the local magnetic moment of the region in which the electrons are situated, this energy is equal to AM, where A is the s-f exchange integral and M is the moment of the region per atom (the exchange energy in the $(1s)^2$ state is equal to zero).

At $T=0$, the local magnetization M is equal to the spin of the magnetic atom S, but it decreases with increasing temperature. Therefore, if the level $(1s)(2s)$ lies lower than $(1s)^2$ at $T=0$, at a certain temperature T_i inversion of the terms can take place, and at higher temperatures the donors will turn out to be in the state $(1s)^2$.

At sufficiently high donor concentration n, owing to the overlap of the electron orbits of the neighboring donor atoms, collectivization of their electrons takes place. The condition for this is the inequality $n^{1/3}r > C$, where r is the radius of the orbit and C is a number of the order of unity (Mott's criterion). It is much easier to satisfy for $(2s)$ electrons than for $(1s)$ electrons, since the radius of the orbits of the former is larger than that of the latter (by a factor of two in the helium-like model). If Mott's criterion is satisfied for $1s$ electrons ($n^{1/3}r_1 > C$), then the system is in the conducting state at all temperatures. On the other hand, if the concentrations lie in the range $n^{1/3}r_2 > C > n^{1/3}r_1$, than at high temperatures the system is an insulator. However, after the term inversion temperature T_i is reached Mott's criterion begins to be satisfied, and the system goes over into a conducting state. Finally, if Mott's criterion is not satisfied even for the $2s$ states ($n^{1/3}r_2 < C$), then the system remains an insulator at all temperatures.

It must be emphasized that the local moment M can differ very strongly from the average magnetization of the crystal. Thus, as $T \to \infty$ the value of M is none other than the fluctuating moment of a region of radius $r \sim r_1, r_2$, and therefore, in accordance with the known statistical-physics result, it is of the order of $S(a/r)^{3/2}$, where a is the lattice constant. The fact that the local moment does not have a fixed direction in space does not affect the electron energies, since their spins in the state $(1s)(2s)$ always become aligned parallel to this moment. If $AS(a/r)^{3/2}$ exceeds E_{12}, the donor remains in the $(1s)(2s)$ state up to the highest temperature. In this case the metal—insulator transition in accordance with the mechanism described above is impossible, but on the other hand it can be effected by the same mechanism as for singly charged donors (see[3-6]).

To calculate the temperature dependence of the energy of a donor state of the type $(1s)(2s)$, the Hamiltonian of the donor is represented in the form

$$\mathcal{H} = \mathcal{H}_0 - A \sum \psi_\nu^*(g)\, \psi_\mu(g)(S_g s)_{\sigma\sigma'}\, a_{\nu\sigma}^*\, a_{\mu\sigma'}, \tag{1}$$

where the Hamiltonian $\mathcal{H}_0$ includes everything except the exchange, S_g and s are the spins of the gth magnetic atom and the conduction electron, respectively, $a_{\mu\sigma}^*$ and $a_{\mu\sigma}$ are the operators for the production and annihilation of an electron in an orbital state with spin projection σ, and $\psi_\mu(g)$ is the orbital part of the single-electron wave function in the node representation. The exchange between the electrons of the donor is very weak and is disregarded.

The wave functions constructed in the form of a linear combination of four states $a_{2s,\sigma}^* a_{1s,\sigma'}^* |0\rangle$, where $|0\rangle$ is the vacuum function. Then in the principal approximation in the s-f exchange we obtain for the part of the energy that depends on the spins of the magnetic atoms

$$E_{sf}\{S\} = -\frac{A}{2}\left\{\sqrt{\overline{\Sigma \psi_{1s}^2(g)\psi_{1s}^2(f)(S_g S_f)}} + \sqrt{\overline{\Sigma \psi_{2s}^2(g)\psi_{2s}^2(f)(S_g S_f)}}\right\}. \tag{2}$$

The quantity E_{sf} is included in the magnetic Hamiltonian of the system, which is therefore not of the Heisenberg type. Up to now, from among all the non-Heisenberg magnetic Hamiltonians describing isotropic interactions, only the biquadratic and the four-spin Hamiltonians have been considered in the literature. The quasilinear Hamiltonian (2) is new.

Since the donor level of the considered type is deep,[2] it can be assumed that the (1s) electron is practically localized on the $z_1 = 6$ oxygen ions of Eu^{++} that are closest to the vacancy, while the 2s electron is localized on the $z_2 = 8$ next in proximity. Then the temperature-averaged exchange shift is represented in the form

$$\bar{E}_{sf} = -\frac{A}{2}\left(\frac{\bar{J}_1}{z_1} + \frac{\bar{J}_2}{z_2}\right), \tag{3}$$

where $\bar{J}_i$ is the total angular momentum of the ith coordination sphere, averaged over the temperature. If the indirect exchange via the electrons in the vicinity of the donor is stronger than the indirect exchange between the magnetic atoms, then at $T \gtrsim T_c$ the averaging is carried out with the aid of the partition function

$$Z_i = \sum_{M=0}^{z_i S} (2M+1) F_i(M) \exp\left\{\frac{AM}{2z_i T}\right\}, \tag{4}$$

where $F_i(M)$ is the number of methods with which it is possible to obtain the total value of the moment M by addition the z_i moment of the quantity S.

From (3) and (4) we find that as $T \to \infty$, when there are no correlations between the spins, E_{sf} amounts to 40% of its value $AS(S=7/2)$ at $T=0$, i.e., in accordance with the estimates given above, it is of the order of $AS/\sqrt{Z}$. Indirect exchange via the donor electrons greatly increase the degree of local order: at $AS = 0.5$ eV and $T = 0.01$ eV (i.e., near the Curie point T_c of EuO), we have $\bar{E}_{sf} \approx 0.9\,AS$. Thus, the energies E_{sf} and E_{12} at all temperatures are of the same order. Therefore both mechanisms described above for the metal—insulator transition in EuO are possible. Additional experiments are necessary to choose between them.

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