SOVIET PHYSICS JETP VOLUME 27, NUMBER 5 NOVEMBER 1968

A NEW TYPE OF AUTO-LOCALIZED STATE OF A CONDUCTION ELECTRON IN AN ANTIFERROMAGNETIC SEMICONDUCTOR

L. N. BULAEVSKII, É. L. NAGAEV, and D. I. KHOMSKIĬ

P. N. Lebedev Physics Institute, U.S.S.R. Academy of Sciences

Submitted December 21, 1967

Zh. Eksp. Teor. Fiz. 54, 1562–1567 (May, 1968)

The motion of an electron is studied in a nondegenerate band of an antiferromagnetic semiconductor, each lattice point of which contains a magnetic electron. If zero-point oscillations are not taken into account, the motion of an extra electron is possible with spin flip and correspondingly with violation of magnetic order along its trajectory. This results in an increase of the magnetic energy as the electron moves away from the center; consequently the ground state is an auto-localized state resembling a magnetic polaron. The upper and lower energy limits of such a state are determined.

GOODENOUGH[1] and de Gennes[2] advanced, within the framework of the sd-model, the idea that in a nonmetallic antiferromagnet a conduction electron can disturb the antiferromagnetic ordering in its immediate vicinity. It was shown in [3] that under certain conditions there is formed around the conduction electron a ferromagnetic microregion, with which it can move over the crystal. Such a quasi-particle was called a magnetic polaron.

To describe many antiferromagnetic substances it is better to use the dd-model, in which, unlike the sd-model, both the magnetic and the electric properties of the crystal are determined by electrons of the same group.[4] In the dd model, if the number of d electrons per magnetic ion is an integer (for example, in Fe_2O_3 but not in Fe_3O_4), then each d electron is localized at a definite atom, owing to the strong Coulomb interaction with the other d electrons. The role of the conduction electrons is played by the d electrons in excess of this number, since they are the ones that can go from atom to atom.

In [4] we investigated the translational motion of the extra d electron in an antiferromagnet under the assumption that it does not change the states of the remaining d-electrons. It was shown under this assumption that the motion of the extra electron over the crystal is possible only as a result of the oscillations of the spins about the equilibrium position. Inasmuch as the amplitude of zero-point oscillations of the spin is small, the gain in the energy of the ground state of the system due to the translational motion of the x-ray electron over the crystal is much smaller than the same value in a nonmagnetic crystal (with the same value of the Bloch integral).

The result of the preceding investigation[4] allows us to state that the considerations advanced in [3] with respect to the energetically favored position of the magnetic-polaron states can be extended also to the dd-model, since in this model they ensure a gain in the kinetic energy of the electron as compared with the case of the undisturbed antiferromagnetic ordering. Three different types of localized electrons state are then possible. The first occurs when the electron moves over a d-level not occupied by the localized state of the electron. This case is perfectly analogous to the sd model considered in [3].

If there is more than one localized d-electron per ion and the extra electron moves over occupied levels (for example NiO, MnO), then a situation similar to the first arises, for in the case of an ideal antiferromagnetic ordering the "extra" electron cannot move, as a result of the Pauli principle, and the "own" electron cannot move as a result of the strong intraatomic exchange (which leads to Hund's rule). Therefore, just as in the first case, the formation of a ferromagnetic microregion around the "extra" electron is energetically favored. On the other hand, the magnetic energy differs in this case somewhat from the case of the sd-model, since the spin at the center, where the "extra" electron is located, differs from the spin of the remaining ions.

The situation in which only the spin of one d-electron is unpaired in the regular magnetic atom, and the landing of the extra d electron on this atom leads to an electronic structure with zero spin (for example, CuO or a hole in VO_2 or Ti_2O_3), calls for special analysis. In this case, too, the magnetic-polaron state would be more favored than the state investigated in [4]. Here, however, the extra electron of the magnetic atom can go over to the neighboring one at any orientation of the spin of the latter, and therefore, in order to obtain the maximum gain in the translational energy, there is no need for losing energy to the creation of the ferromagnetic microregion. It will be shown below that in such a situation the extra electron is in an autolocalized state of a different nature.

Assume that an additional electron appears at the magnetic atom in an antiferromagnet. With further motion of the excess charge through the crystal, if we neglect the zero-point oscillations of the spins, the transition from this atom to the neighboring one should be executed by that electron, whose spin is opposite to the spin of the neighbor, (i.e., the former "own" electron of the atom). The electron remaining in the same atom has a spin opposite to the initial spin of the atom (the former "extra" electron). Since each such spin flip of the atoms by the excess charge passing through them is accompanied by an increase of the energy of the exchange interaction of the electrons, this extra charge cannot propagate freely through the crystal and becomes auto-localized. The center of the auto-localized state is the atom on which the extra electron lands without causing the spins of the remaining atoms to lose the ideal antiferromagnetic ordering. As the electron moves away from the center, flipped spins appear on its trajectory, and the exchange energy increased with lengthening of the trajectory. This can be interpreted as the existence of a quasi-elastic force that tends to return the extra electron to the center. Thus, the auto-localized electron is to a certain degree the analog of a three-dimensional oscillator, and we shall use the term "quasi-oscillator" to denote this state.

The quasi-oscillator state differs essentially from the polaron state. In the latter, the deformation of the captured subsystem (crystal lattice[5] or spin system[2, 3]) exists at all possible positions of the conduction electron. In a magnetic-polaron state, this leads to a non-zero magnetic moment of the microscopic region in which the electron is localized. On the other hand, in the quasi-oscillator state violation of the magnetic ordering occurs only when the electron moves away from the center, and the character of this violation is such that no additional magnetic moment appears here.

We shall consider below the ground state of a resting quasi-oscillator. We assume for simplicity that there can be not more than two electrons per atom, so that the state of the electron is characterized by the number of the magnetic atom g and by the spin projection σ. As in [4], we describe the system in the isotropic case by the Hamiltonian

$$H = H_0 + H', \quad H' = \sum_{\langle g, g'\rangle, \sigma} \beta a^+_{g\sigma} a_{g'\sigma}, \tag{1}$$

$$H_0 = {}^1/_2 \sum_{g_1, g_2, \sigma_1, \sigma_2} U(g_1, g_2) a^+_{g_1\sigma_1} a_{g_1\sigma_1} a^+_{g_2\sigma_2} a_{g_2\sigma_2}.$$

Then the system with the extra electron (or hole) in the zeroth approximation in H′ will be $N2^{N-1}$-fold degenerate (N—total number of magnetic atoms). This degeneracy is lifted by the term H′, and accurate to second order in H′ inclusive, we obtain the secular equation with the effective Hamiltonian

$$H_{\text{eff}} = PH'P + PH' \frac{1-P}{H_0 - E} H'P$$
$$= \sum_{\langle g, g'\rangle, \sigma} \beta P a^+_{g\sigma} a_{g'\sigma} P + J \sum_{\langle g_1, g_2\rangle, \sigma_1, \sigma_2} P a^+_{g_1\sigma_1} a_{g_2\sigma_1} (1-P) a^+_{g_2\sigma_2} a_{g_1\sigma_2} P,$$
$$J = \beta^2 / [U(0, 0) - U(0, 1)], \tag{2}$$

where P is the operator of projection on the space of the $N2^{N-1}$-fold degenerate functions of the system with the "extra" electron. The first term in (2) describes the transitions of the "extra" electron to the neighboring centers, and the second describes the magnetic interaction of the localized electrons due to the indirect exchange. All the centers, except that occupied by the "extra" electron, take part in the exchange, and the spin on the occupied center is zero. This is taken into account by the operator 1 − P in (2). The second term in (2) leads also to transitions of the "extra" electron to centers that follow the nearest neighbors. We shall neglect them compared with the transitions to the nearest centers, since $J \ll \beta$.

In the absence of the extra electron, the Hamiltonian (2) reduces to the Heisenberg Hamiltonian.[6, 7] We shall assume that in the absence of an extra electron the Hamiltonian (2) leads to antiferromagnetic ordering, and we neglect the zero-point oscillations of the spins. Then, in accordance with the foregoing, the wave function of the system can be represented in the form

$$\Phi = \sum_l C'[l] | l\rangle, \quad C'[l] \equiv C'(g_n, \ldots, g_1, g_0),$$
$$| l\rangle = a^+_{g_n, \sigma_n} a_{g_{n-1}, \sigma_n} a^+_{g_{n-1}, \sigma_{n-1}} \cdots a^+_{g_2, \sigma_2} a_{g_1, \sigma_2} a^+_{g_1, \sigma_1} a_{g_0, \sigma_1} a^+_{g_0, -\sigma_0} | 0\rangle. \tag{3}$$

Here l—trajectory of the "extra" electron, $l = \{g_0, g_1, \ldots, g_n\}$; $|0\rangle$—wave function of the ground state of the antiferromagnetic (without the extra electron). The proper electron of the central atom g_0 has a spin projection σ_0. The set of spin indices σ_k is determined by the following rule: $\sigma_1 = \sigma_0$; if the trajectory crosses itself on the k-th step, then $\sigma_k = \sigma_{k-1}$, in all other cases $\sigma_k = -\sigma_{k-1}$. The summation over g_k in (3) is limited by the condition that the atom with number g_k be the nearest neighbor of the atom g_{k-1}, but must not coincide with g_{k-2}.

From (2) and (3), with allowance for the orthogonality of the states for the different trajectories, we obtain the energy of the system

$$\mathscr{E} = \beta \sum_{\langle l, l'\rangle} C'[l'] C'[l] + \sum_l E_l (C'[l])^2, \tag{4}$$

where the trajectory l' differs from l by a continuation through one step, E_l—magnetic energy of the flipped spins on the trajectory l. In the three-dimensional lattice, for trajectories without self-intersections and self-tangencies, $E_l = 2J(z-2)n + 2J$, where n—number of steps on the trajectory l, and z—number of nearest neighbors. On the other hand, the energy of the trajectories of the same length with self-intersections and (or) self-tangencies is smaller.

We shall show first that the energy of the magnetic quasi-oscillator state is smaller than the energy of the electron calculated in [4]. To this end we use a variational method, confining ourselves in (3) and (4) to trajectories in which the number of steps does not exceed three. There are no self-intersecting trajectories in this case, but there is one type of trajectory with self-tangency. Calculation yields

$$\mathscr{E} \approx -3{,}7\beta + 22J. \tag{5}$$

From expression (5) we see that when $J \ll \beta$ this value of the energy, being too high compared with the true value, is nevertheless lower than the value of the energy of the states obtained in [4].

We obtain now an approximate solution of the problem such that it gives a lower estimate for the energy of the ground state of the quasi-oscillator. To this end, we break down all the trajectories into groups with fixed final point g. Such trajectories will be denoted l_g. It is convenient to make the substitution $C'[l_g] = \psi_g C[l_g]$ such that

$$\sum_{l_g} (C[l_g])^2 = 1. \tag{6}$$

The summation in (6) is over all the trajectories that emerge from the point 0 and terminate at the point g. The quantity ψ_g is the amplitude of the probability of finding the extra electron in the site, independent of the path taken to reach the site. It is the exact analog of the ordinary wave function with discrete representation for the Schrödinger equation with the ordinary potential that depends only on the point but not on the trajectory. In this notation, the energy (4) becomes

$$\mathscr{E}=\beta\sum_{\langle g,g'\rangle}\psi_g\psi_{g'}\sum_{l_g l'_{g'}}C[l_g]\,C[l_{g'}']+\sum_g(\psi_g)^2\sum_{l_g}E_{l_g}(C[l_g])^2. \tag{7}$$

We now replace in the second term of (7) the values of the energy by the smaller values $K_g = 2J(z-2)m_g$, where m_g is the smallest number of steps that lead to the point g (K_g—energy of the shortest trajectory leading to the point g; the values of the energy E_l on the remaining trajectories are larger than K_g). When such a substitution is made, all the trajectories leading to the point g become equivalent, and for each point $C[l_g] = \text{const} = 1/\sqrt{L_g}$, where L_g is the total number of trajectories leading to the point g. We shall now show that $L_g = L_{g'}$. Indeed, any trajectory leading to the point g can be continued into the neighboring point g′, by making one more step, in a unique manner. At the same time, each trajectory leading to g′ can be uniquely set in correspondence with a trajectory leading to g and differing from the initial one only by a single step from g′ to g. Thus, we can establish a mutually-unique correspondence between the trajectories leading to two neighboring points: consequently, the total number of such trajectories is the same, $L_g = L_{g'}$. Hence $C[l_g] = C[l_{g'}] = 1/\sqrt{L_g}$ and by using (6) we get

$$\mathscr{E}=\beta\sum_{\langle gg'\rangle}\psi_g{}^*\psi_{g'}+\sum_g K_g(\psi_g)^2. \tag{8}$$

When $\beta \gg J$ we can go over to the approximation of the continuous medium and obtain for a cubic crystal, from (8), the equivalent Schrödinger equation

$$-\beta\Delta\psi(\mathbf{r})-6\beta\psi(\mathbf{r})+8Jr\psi(\mathbf{r})=E\psi(\mathbf{r}). \tag{9}$$

For the s-wave Eq. (9) reduces to the Airy equation, and the energy of the ground state is

$$\mathscr{E}=-6\beta+9{,}32\beta^{1/3}J^{2/3}. \tag{10}$$

We note that in the case of a strongly anisotropic crystal (for example, of the VO_2 type), in which the Bloch integral β_x for the neighbors along the x axis is large compared with β_y and β_z, the motion of the electron can be regarded as one-dimensional. At the same time, the exchange integrals J_y and J_z will be assumed to differ from zero, for in the other case there would be no magnetic ordering. In this case the one-dimensional equation analogous to (9) turns out to be exact, since the magnetic energy depends here only on the final point of the trajectory $E_{lg} \equiv E_g = (J_y + J_z) \times (z-2)g + 2J_x$. The corresponding values of the ground-state energy is in this case

$$\mathscr{E}=-2\beta_x+1.02\beta_x^{1/3}[(J_y+J_z)(z-2)]^{2/3}. \tag{11}$$

The occurrence of an auto-localized quasi-oscillator state leads to the formation of a region with partial disorder near the center of its localization. Using the approximation equation (9), we can estimate the value of the magnetic moment produced at the sublattice site by a single extra electron in the quasi-oscillator state. The change in the average spin of the site located at a distance R from the localization center is

$$\Delta\langle S_R{}^z\rangle=\frac{1}{4\pi R^2}\int_{|\mathbf{r}|>R}\psi^2(\mathbf{r})\,d\mathbf{r}, \tag{12}$$

Since the spin-flip probability at a given site is equal to the probability of the emergence of the x-ray electron to the outside of a sphere of radius R through this site. Averaging of this expression over the position of the localization center of the quasi-oscillator gives at an extra-electron concentration n

$$\Delta\langle S^z\rangle\approx n\int_0^\infty dR\int_{|\mathbf{r}|>R}\psi^2(\mathbf{r})\,d\mathbf{r}\approx n(\beta/J)^{2/3}. \tag{13}$$

So far we have considered only the localized state of the quasi-oscillator. Such states with centers at different lattice sites are equivalent, and therefore the quasi-oscillator should move over the lattice. It is easy to verify, however, that if we confine ourselves to the considered class of functions (3) and do not take into account the zero-point oscillations, then, in analogy with [4], in first order in H′ there will be no transitions from center to center, since

$$\langle\Phi_g|H'|\Phi_{g'}\rangle=0 \text{ for } g\neq g',$$

where Φ_g is the wave function of the quasi-oscillator (3) with center at the site g.

Our analysis was limited to the case T = 0. It is clear that when $T > T_N$ the antiferromagnetic ordering vanishes, and the quasi-elastic force localizing the electron vanishes with it. Therefore we can expect that when $T \gg T_N$ the extra electron will move over the lattice freely, with minimum energy (-6β). Thus, on going through the Neel point, the minimum excitation energy decreases by an amount $\approx \beta^{1/3}J^{2/3}$. This result, in a somewhat different model, is analogous to the result obtained in [4], and can be connected with the experimental data on the change of the energy gap in a number of antiferromagnetic semiconductors on going through the Neel point.[8, 9]

In conclusion, we are grateful to L. V. Keldysh for a useful discussion.

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Translated by J. G. Adashko
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