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THE ELECTRICAL CONDUCTIVITY OF ANTIFERROMAGNETS

L. N. BULAEVSKIĬ and D. I. KHOMSKIĬ

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

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The Fermi excitation spectrum in antiferromagnets of the transition-metal-oxide type is studied as a function of the magnetic ordering. It is shown in the localized-electron model that because of the Pauli principle the electron and hole bands are much narrower in the ordered state. A strong broadening of the bands and hence a decrease in the energy gap occurs above the Néel point. The results obtained can explain the observed dependence of the electrical conductivity on the magnetic structure in substances of the NiO type.

1. IN this paper we study the structure of the electronic spectrum of antiferromagnetic semiconductors of the transition-metal-oxide type (e.g., NiO, CoO, Fe_2O_3). It is characteristic of this class of substances that the very same d electrons are responsible for both the magnetic and the electrical properties. Hence it is natural to expect that the structure of the d band should be closely associated with the magnetic ordering.

The substances in this class are ionic crystals. The separation between the transition-metal ions in them is large, and consequently the overlap of the d functions of different ions may be neglected. The delocalization of the d electrons is due to indirect exchange;[1] it is small, and in the calculation it is necessary to start from the localized electron model.

We shall first consider the case when the atomic wave functions are nondegenerate (e.g., the hydrogen s-level) and there is but one electron per center. The complexities brought about by the fivefold degeneracy of the d-level will be introduced later.

Using the localized Wannier functions as a basis, we write the Hamiltonian of the electrons in the form

$$H = \beta \sum_{\langle n_1 n_2\rangle,\sigma}' a^+_{n_1\sigma} a_{n_2\sigma} + {}^1/_2 \sum_{n_1 n_2} U_{n_1 n_2} \rho_{n_1} \rho_{n_2} = H' + H_0,$$

$$\rho_n = \sum_\sigma a_{n\sigma}{}^+ a_{n\sigma}. \tag{1}$$

Here $a^+_{n\sigma}$ is the creation operator for an electron with spin σ at site n; β is the matrix element of the transition of the electron to a neighboring center due to indirect exchange, and the symbol $\langle n_1 n_2\rangle$ in the first term H′ of the Hamiltonian indicates summation over nearest neighbors. The second term H_0 describes the Coulomb interaction of the electrons. All the remaining terms of the interaction, which contain integrals of the Wannier function of different centers, are small and may be left out.[1]

The characteristic parameter of the Coulomb interaction is the quantity $U = U_{00} - U_{01}$. For the given substances, $U \approx 6$ eV and $\beta \approx 0.3$ eV. In this case it is possible to treat H′ as a perturbation, taking H_0 as the zero-order Hamiltonian. In the ground state of H_0 there is one electron per center; this state is 2^N-fold degenerate with respect to spin (N is the total number of centers); its energy is E_0. This degeneracy is lifted in second order with respect to H′; the effective Hamiltonian of the corresponding secular equation can be reduced to the Heisenberg Hamiltonian with antiferromagnetic interaction

$$H_{\text{eff}} = \frac{4\beta^2}{U} \sum_{\langle n_1 n_2\rangle} \mathbf{S}_{n_1} \mathbf{S}_{n_2}. \tag{2}$$

The Schrödinger equation with the Hamiltonian (2) determines the stationary linear combinations $|\alpha\rangle$; from them one determines the wave functions of these states:

$$|\Phi_\alpha\rangle = \left(1 - \frac{H'}{H_0 - E_0}\right)|\alpha\rangle. \tag{3}$$

We shall assume that the ground state $|\Phi_0\rangle$ of the Hamiltonian (2) is antiferromagnetic. With this assumption it is possible to calculate the average values of the spin operators in the ground and excited states of the Hamiltonian (2).[2]

2. Let us consider the structure of the spectrum of the single-particle Fermi excitations of the sys-

tem. Such excitations can be obtained by transferring an electron from the center n_1 (a hole at the center n_1) to the same level of center n_2 (an excess electron at n_2) and considering the case when the electron and hole thereafter move independently, without forming a coupled pair of the exciton type. In the zeroth approximation this state is separated from the ground state by a gap U—the repulsive energy of two electrons at one center, and the substance is a dielectric.

Our system corresponds to the dielectric phase of the model proposed by Hubbard[3] for treating the Mott dielectric-metal transition.

We symbolize the energy of the electron by ϵ_e and that of the hole by ϵ_h; from the above it is clear that in the zeroth approximation $\epsilon_e - \epsilon_h = U$ and the state with the excess electron or hole is N-fold degenerate. The term H′ lifts the degeneracy, leading to delocalization of the electrons and washing out the electronic and hole levels in the band.

The spectrum of elementary excitations is determined by the poles of the single-particle Green function

$$G_{n_1\sigma_1 n_2\sigma_2}(\tau) = i\langle T\overset{+}{\tilde{a}}_{n_1\sigma_1}(\tau)\tilde{a}_{n_2\sigma_2}(0)\rangle,$$

$$\overset{+}{\tilde{a}}_{n\sigma}(\tau) = e^{i\tau(H_0+H')}\overset{+}{a}_{n\sigma}e^{-i\tau(H_0+H')}. \tag{4}$$

Averaging here is understood both in the quantum-mechanical and in the statistical sense, i.e.,

$$\langle\ldots\rangle = \sum_n \langle\Phi_n|e^{-H/kT}\ldots|\Phi_n\rangle \Big/ \sum_n \langle\Phi_n|e^{-H/kT}|\Phi_n\rangle.$$

To determine the spectrum it is necessary to find the mass operator M; the spectrum is given by the solution of the equation

$$1 - G^{(0)}M = 0. \tag{5}$$

The mass operator is calculated in the first order of the perturbation H′, utilizing the fact that the first-order correction to the Green function is

$$G^{(1)} = G^{(0)}MG^{(0)}.$$

Having calculated $G^{(1)}$ we shall solve, instead of (5), the following equation, which is equivalent to it:

$$G^{(0)} - G^{(1)} = 0. \tag{6}$$

Since the ground state of the Hamiltonian H_0 is degenerate, the standard technique of perturbation theory in the interaction representation is not applicable to the problem of calculating the Green function. In the Heisenberg representation, which we shall use, it is necessary to carry out the averaging in (4) over the eigenfunctions of the total Hamiltonian H, taken in corresponding order; in zeroth order with respect to H′ for the degenerate states these are the true linear combinations $|\alpha\rangle$, determined by solving the secular equation with the Hamiltonian (2), and in first order they are the functions $|\Phi_\alpha\rangle$ given by Eq. (3).

In expanding the Heisenberg operators in a series in H′ we use the formula[4]

$$e^{\tau i(H_0+H')} = e^{i\tau H_0} + i\int_0^\tau e^{i(\tau-t)H_0}H'e^{itH_0}\,dt + o(H'). \tag{7}$$

In the statistical average it is necessary, for the degenerate states, to use in the exponential their energies E_α, found after the degeneracy is lifted, so that

$$e^{-H/kt}|\Phi_\alpha\rangle = e^{-E_\alpha/kT}|\Phi_\alpha\rangle,$$

and it is possible to omit from the average all states other than $|\Phi_\alpha\rangle$, since all such states are separated from the ground state by the energy gap $U \gg \beta$.

Substituting (3) and (7) into (4), separating out the terms of zeroth and first order in β, and carrying out a Fourier time transformation, we obtain

$$G^{(0)}_{n_1\sigma_1\, n_2\sigma_2}(\varepsilon) = \left[\frac{\delta_{\sigma_1\sigma_2} - K_2(n_1, \sigma_1\sigma_2)}{\varepsilon - \varepsilon_e + i\delta} + \frac{K_2(n_1\ \sigma_1\sigma_2)}{\varepsilon + \varepsilon_h - i\delta}\right]\delta_{n_1 n_2}, \tag{8}$$

$$G^{(1)}_{n_1\sigma_1\, n_2\sigma_2}(\varepsilon) = \frac{\beta}{U}[\delta_{\sigma_1\sigma_2} - 2K_4(n_1n_2, \sigma_1\sigma_2)]\left(\frac{1}{\varepsilon - \varepsilon_e + i\delta} - \frac{1}{\varepsilon + \varepsilon_h - i\delta}\right) + \frac{\beta K_4(n_1n_2, \sigma_1\sigma_2)}{(\varepsilon - \varepsilon_e + i\delta)^2} - \frac{\beta K_4^+(n_1n_2, \sigma_1\sigma_2)}{(\varepsilon + \varepsilon_h - i\delta)^2}. \tag{9}$$

Here n_1 and n_2 are nearest neighbors, and K_2 and K_4 are correlation functions given by the statistical averages over the spin functions $|\alpha\rangle$ from the quadratic and quartic forms of the Fermi operators, respectively:

$$K_2(n, \sigma_1\sigma_2) = \langle\overset{+}{a}_{n\sigma_1}a_{n\sigma_2}\rangle, \tag{10}$$

$$K_4(n_1n_2, \sigma_1\sigma_2) = \left\langle\sum_\sigma \overset{+}{a}_{n_1\sigma_1}a_{n_1\sigma}\overset{+}{a}_{n_2\sigma}a_{n_2\sigma_2}\right\rangle. \tag{11}$$

All the elements of $G^{(1)}$ for other than nearest neighbors are zero. When the spin functions $|\alpha\rangle$ are acted upon, we have

$$\overset{+}{a}_{n,\pm 1/2}a_{n,\pm 1/2} = 1/2 \pm S_n^z, \quad \overset{+}{a}_{n,\pm 1/2}a_{n,\mp 1/2} = S_n^\pm. \tag{12}$$

Using (12) and taking into account that after the averaging, the elements of the correlators that are non-diagonal in the spins vanish owing to the conservation of the spin projection, we find

$$K_2(n, \sigma_1\sigma_2) = \begin{pmatrix} 1/2 + s_n & 0 \\ 0 & 1/2 - s_n \end{pmatrix}, \tag{13}$$

$$K_4(n_1n_2,\sigma_1\sigma_2)=\delta_{\sigma_1\sigma_2}K_{n_1n_2}=\delta_{\sigma_1\sigma_2}({}^1/{}_4+\langle\mathbf{S}_{n_1}\mathbf{S}_{n_2}\rangle). \quad (14)$$

Here

$$s_n=\langle S_n^z\rangle,$$
$$\langle\mathbf{S}_{n_1}\mathbf{S}_{n_2}\rangle=\langle S_{n_1}^zS_{n_2}^z+S_{n_1}^{\pm}S_{n_2}^{\mp}\rangle.$$

We have also made use of the fact that in the antiferromagnetic state we have for the nearest neighbors $s_{n_1}+s_{n_2}=0$.

It can be seen from (8), (9), (13), and (14) that the elements in Eq. (6) which are non-diagonal in the spin indices vanish and the diagonal ones are equivalent, and we can limit ourselves to considering an equation for only one spin direction. Then to first order in β Eq. (6) for the spectrum of the electrons (holes) reduces to

$$\|\beta K_{n_1n_2}-\delta_{n_1n_2}({}^1/{}_2-s_{n_1})(\varepsilon-\varepsilon_{e(h)})\|=0. \quad (15)$$

We diagonalize the matrix (15) by a Fourier transformation with respect to the space indices n_1 and n_2, taking into account that $s_n=\pm s$ for the sites of the different sublattices. Setting the diagonal elements equal to zero, we obtain the electron (hole) spectrum for the simple cubic lattice

$$\varepsilon_{e(h)}(\mathbf{k})=\varepsilon_{e(h)}+2\beta\varphi(T)(\cos k_x+\cos k_y+\cos k_z),$$
$$-\pi\leqslant k_x,k_y,k_z\leqslant\pi. \quad (16)$$

Here

$$\varphi(T)=\frac{{}^1/{}_4+\langle\mathbf{S}_0\mathbf{S}_1\rangle}{\sqrt{{}^1/{}_4-s^2}} \quad (17)$$

is a factor describing the effect of the magnetic ordering on the band structure. Thus we see that by taking overlap into account (the term H′) the degenerate levels of the Fermi excitations of the system are diffused into bands. It is significant that the width of these bands depends on the magnetic ordering. This is because the probability of a transition from center to center, which is proportional to the matrix element of the transition β, is limited by the Pauli principle.

When there is stable antiferromagnetic ordering, only an electron with the opposite spin $-{}^1/{}_2$ can transfer to a given center with spin $+{}^1/{}_2$, but then there are electrons with spin $-{}^1/{}_2$ at the neighboring centers, and consequently the transfer of the extra electron to them is forbidden. "Zero-point vibrations" at $T=0$ and thermal disordering at $T\neq 0$ make these transitions possible, but it is clear that when $T<T_N$ they are still suppressed to a large extent, and the bands are narrow. Mathematically this effect is indeed described by the factor $\varphi(T)$, into which enter the correlation functions of short-range order $\langle\mathbf{S}_0\mathbf{S}_1\rangle$ and the average moment of the sublattice s, which describes long-range order. The single-particle spectrum depends on temperature through these correlators. The influence of the Pauli principle on the electrical properties of antiferromagnets has also been discussed on the basis of a somewhat different model in [5].

The results of (16) and (17) can also be obtained by the usual perturbation theory for a degenerate level; however, in this method it is difficult to justify the use of temperature-dependent correlators.

Let us consider the temperature dependence of the correlators appearing in (17). The correlator $\langle\mathbf{S}_0\mathbf{S}_1\rangle$ is proportional to the average magnetic energy of one center (see Eq. (2)), and the factor $\varphi(T)$ can be evaluated from experimental data (e.g., from the heat capacity and the magnetic scattering of neutrons). Obviously, the sharpest change in the correlator $\langle\mathbf{S}_0\mathbf{S}_1\rangle$ occurs in the vicinity of T_N, since the heat capacity is infinite at the Néel point.

The value of $\varphi(T)$ can also be estimated starting from theoretical calculations for the Hamiltonian (2). At $T=0$ we have $\langle\mathbf{S}_0\mathbf{S}_1\rangle=-0.295$, $s=0.43$,[2] and $\varphi(0)=-0.18$. As the temperature is raised, the correlator $\langle\mathbf{S}_0\mathbf{S}_1\rangle$ increases, and there is a point where $\varphi(T)=0$. Near this point it is necessary to take into account the terms of higher order in β/U that were left out earlier. These terms lead to a finite width of the conduction band, of the order of $10\beta^2/U$, near this point.

When $T\gg T_N$, we have $s=0$, $\langle\mathbf{S}_0\mathbf{S}_1\rangle\approx T_N/T$, and $\varphi(T)\to{}^1/{}_2$. It is interesting that unlike the purely single-particle scheme, the factor $\varphi(T)$ in the disordered phase is equal to ${}^1/{}_2$, not 1. This is due to the presence at each center, with probability ${}^1/{}_2$, of an electron with the same spin as that of the extra electron.

The general appearance of the spectrum is shown schematically in Fig. 1. The upper band is the electron band, the lower band is the hole band. We see that the forbidden zone narrows sharply near the Néel point in the transition to the disordered phase.

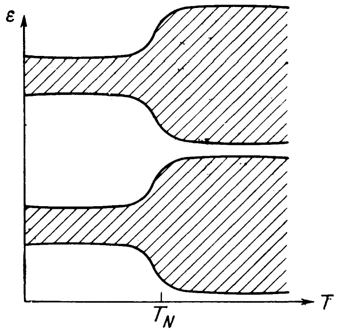

FIG. 1.

This model can qualitatively explain the connection between the electrical and the magnetic properties of substances in which the magnetic ordering is due to indirect exchange and the conductivity is effected via the d band. The narrowing of the forbidden zone above the Néel point that is obtained in several experiments[6-9] is evidently explained by the effect considered above.

3. In real cases one must take account of the complications associated with the degeneracy of the d band and with the fact that in general there is more than one d electron per center. The fivefold degeneracy of the d level of an isolated ion in a crystalline field of cubic symmetry is partially lifted, and we obtain a threefold degenerate level t and a twofold degenerate level e_g lying about 1 eV above level t.[10] In this connection we must keep in mind, first of all, that the electron can move over an unoccupied level. In addition, if there is more than one d electron at each ion, their exchange interaction must be considered; this leads, first, to a total spin of the electrons at each center of $S \geq 1/2$, and, second, to an additional splitting of the electron and hole bands when $T < T_N$.

In the case of a degenerate band the Pauli principle prohibits the motion of an electron when $T < T_N$. This leads to a narrowing of the conduction band in the antiferromagnetic state. In the d band, if the number of d electrons is less than the number of degenerate levels (for example, if there is only one d electron in a t state and two t levels are free), the extra electron can travel over free levels with the same energy, and the Pauli principle does not prohibit its movement. In this case the width of the electron band is independent of the spin ordering, and the factor φ in (16) is equal to 1. It is not difficult to see that with this structure of the d bands in cubic crystals the effect of narrowing of the electron band below the Néel point will occur when the number of d electrons $n = 3.5-9$. Similar considerations for the holes show that the corresponding effect for the holes will take place when $n = 1-5.8$. Hence it is clear that this effect should occur always for intrinsic conductivity, and depending on the type of conduction and the number of d electrons for impurity conductivity.

The exchange interaction of the d electrons at one center when $n > 1$ is not small, and we need to take account of it already in the zeroth order of perturbation theory. It leads to the fact that the total spin S at each center $S = n/2$ for $n \leq 5$, and $S = 5 - (n/2)$ for $n \geq 5$ (Hund's rule). To the electron creation and annihilation operators it is necessary to assign an index α, the number of the d level ($\alpha = 1, 2, \ldots, 5$). We shall work in the representation in which the matrix element of the transition $\beta_{\alpha\alpha'}$ in (1) is diagonal in α. In this case both the single-particle Green functions (8) and (9) and the correlators K_2 and K_4 also need to carry the index α. Since all singly-filled d levels enter into the spin functions identically,

$$K_{2(4)\alpha} = \frac{1}{2S} \sum_{\alpha'} K_{2(4)\alpha\alpha'}. \tag{18}$$

The sum in (18) now coincides, respectively, with the right part of Eqs. (13) and (14), in which the operators for spin $1/2$ are replaced by the operators for spin S. As a result

$$\varphi(T) = \frac{1}{2S} \frac{S^2 + \langle S_0 S_1 \rangle}{\sqrt{S^2 - s^2}}. \tag{19}$$

For large values of S we have $\varphi(0) \sim S^{-1/2}$,[2] i.e., the narrowing effect is stronger the bigger S is.

For $n > 1$, inclusion of the exchange interaction in zeroth approximation leads for $T < T_N$ to a splitting of the excitation spectrum depending on spin direction:

$$\varepsilon_e^{1,2} = \varepsilon_e \pm \frac{1}{2} J (2S - 1) \frac{s}{S}, \tag{20}$$

where J is the magnitude of the exchange interaction of two electrons at one site. A similar formula also exists for the holes. Then, from (15) and (20), we obtain

$$\varepsilon_{e(h)}^{1,2}(\mathbf{k}) = \varepsilon_{e(h)} \pm [4\beta^2 \varphi^2(T) (\cos k_x + \cos k_y + \cos k_z)^2 + J^2 (1 - 1/2S)^2 s^2(T)]^{1/2}. \tag{21}$$

Here $-\pi/2 \leq k_x, k_y, k_z \leq \pi/2$. If the extra electron moves over an unoccupied level, it is necessary to replace $2S - 1$ by $2S$ and set $\varphi(T) = 1$ in Eqs. (20) and (21).

The splitting of the band is associated with a magnetic doubling of the period. This effect was considered in [11, 12] with no account taken of the Pauli principle. For intrinsic conductivity it always leads to an increase in the gap in the disordered phase. It is clear from (21) that in fact the resulting effect depends on the ratio of the parameters β and J. The form of the spectrum for $6\beta > J(2S - 1)$ is shown schematically in Fig. 2.

With increasing spin the effect of exchange splitting of the d band becomes stronger and may become predominant. This is apparently the situation in CoO.[13]

For comparison with experiment it is necessary to further consider the polarization of the lattice. The results of Giterman and Irkhin[12] show that the main part of the electron-phonon interaction, diagonal in the number of electrons at the center,

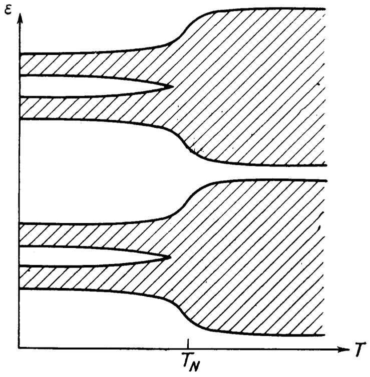

FIG. 2.

leads to a decrease in the gap, independently of the magnetic ordering; the nondiagonal part of this interaction (the term K_1 in [12]), on the other hand, is small.

The experimental data on the conductivity of antiferromagnetic semiconductors is most complete for NiO. In the most careful recent work[6,7] a jump in the activation energy is obtained at the Néel point, corresponding to a narrowing of the forbidden zone when $T > T_N$. For intrinsic conductivity the gap changes typically by 0.2 to 0.3 eV and in the case of Li impurity by 0.1 to 0.15 eV.

In NiO there are eight d electrons, and the narrowing effect occurs both in the electron and in the hole band, so that the change in the gap in intrinsic conductivity should actually be twice as great as in impurity conductivity. It is difficult to give a numerical prediction of the magnitude of the change, since it is the difference between two large magnitudes that are known only to an order of magnitude. According to Anderson,[1] $J \approx 1-1.5$ eV and $\beta \approx 0.3$ eV in NiO ($S = 1$). Our treatment (Eq. (21)) gives for these values of the parameters a decrease in the gap above T_N of 0.3 to 0.8 eV.

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