Phase separation and resistivity jumps in Co compounds and other materials with low-spin - high-spin transitions

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Abstract. States of charge carriers in transition metal compounds with low-frequency zero-spin–nonzero-spin transitions (e.g. some Co compounds) are investigated. Such transitions indicate the appearance of magnetic excitons on the transition metal ions. Charge carriers interact strongly with the excitons via exchange forces. As a result, magnetoexcitonic self-trapping of carriers (holes) is possible in the ions when a complex consisting of a hole and one or several magnetic excitons arises. According to the parameters of the system, the magnetic ordering in the complex may be either collinear ferromagnetic or antiferromagnetic, or indeed canted antiferromagnetic. In the ground state of degenerate semiconductors, spontaneous separation into magnetoexcitonic and nonmagnetic phases is possible, with all of the holes concentrated in the former phase. The same magnetic structures are allowed in the ground state as in the hole–exciton complexes. On increase of the hole density, percolation of holes and magnetic excitons takes place, which leads to a transition from the insulating phase-separated state to the highly conducting phase-separated state.

1. Introduction

A class of transition metal compounds exists in which the d shells of transition metal ions are filled only partially but, nevertheless, these ions are nonmagnetic. The reason for this is the crystalline field which causes violation of Hund's rule for the ions inside the crystal. This rule, requiring the maximum possible magnitude of the d-shell spin, is a consequence of the fact that the exchange interaction between electrons of the same d shell tends to align their spins parallel to each other. But the crystalline-field splitting of d levels may exceed the corresponding exchange energy, and then Hund's rule is valid not for the whole d shell but only for each crystalline-field component separately.

As an example, crystals containing Co^{3+} ions will be considered. The fivefold orbitally degenerate d level is split into a threefold degenerate t_{2g} level and a twofold degenerate e_g level. The Co^{3+} ground state is the singlet $^1A_{1g}(t_{2g}^6)$ with all six d electrons occupying the lowest t_{2g} component and with no electrons on the e_g level. But the excited spin-2 $^5T_{2g}(t_{2g}^4e_g^2)$ state with total spins of both the t_{2g} and e_g subshells equal to 1 usually lies very close to the singlet (from 0.01 to 0.08 eV [1]). Thus, this state may be treated as a low-frequency magnetic exciton. For example, in $LaCoO_3$ the exciton energy is 0.02 eV according to [2] and 0.05 eV according to [3]. Similar properties are displayed by $HoCoO_3$ [4] and Co_2O_3 [5].

Usually such materials are p semiconductors. Two types of hole state are possible: the hole may move over magnetic Co ions or over nonmagnetic (e.g. oxygen) ions. The

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quantitative results are the same in the two cases. For the sake of definiteness, the former case will be considered.

If charge carriers appear in such a crystal, their interaction with magnetic excitons becomes crucial. The main part of this interaction is the hole– (or electron–) exciton exchange which is very strong when the carrier and exciton are located on the same d ion (their exchange integral may be of the same order of magnitude as that for the d electrons of the same ion, i.e. it may reach 10 eV). For this reason each magnetic exciton may trap a carrier and, hence, reduce its energy.

Moreover, the energy of a nondegenerate semiconductor containing free carriers may be reduced even in the absence of prefabricated excitons if one creates one magnetic exciton or their complex especially for their trapping of a carrier. Then the energy spent in the creation of the magnetic excitons will be compensated by the energy gain resulting from the trapping of carriers by excitons. In the case of the exciton complex one may speak of a self-trapped state of a charge carrier inside a region occupied by excitons. Such a state resembles the charge-carrier self-trapping inside regions of a changed magnetic phase, e.g., inside ferromagnetic regions in an antiferromagnetic semiconductor [6, 7].

But there is an essential difference between the self-trappings in these two cases. First, the magnetoexcitonic regions are not necessarily ferromagnetically ordered. They may be ordered in some other way, e.g., antiferromagnetically, and the canting of sublattice moments is possible. Second, the fourfold-occupied t_{2g} subshells in the excited state $^5T_{2g}$ are orbitally degenerate. This causes the tendency towards the Jahn–Teller effect which lowers the energy of the excited ion due to the lifting of this degeneracy. It is essential that the Jahn–Teller effect should be found not throughout the entire crystal but only in the region where magnetic excitons are induced by a charge carrier. Thus, unlike the situation discussed in [6, 7], here the self-trapped charge carrier not only changes the magnetic state of the self-trapping region, but also causes its crystallographic distortion.

For degenerate semiconductors, in full analogy with degenerate antiferromagnetic semiconductors for which numerical calculations were carried out in [8, 7], one may expect that in the materials considered the carrier self-trapping is a cooperative phenomenon. It is energetically favoured in the ground state of the degenerate semiconductor for all of the charge carriers to be concentrated inside the magnetoexcitonic phase. The portion of the crystal outside the excitonic phase is insulating and nonmagnetic, i.e. charge-carrier-induced phase separation of the crystal takes place.

As the magnetoexcitonic and nonmagnetic phases are charged oppositely, the Coulomb forces arise in the phase-separated system under consideration. To diminish the Coulomb energy, the phases tend to intermix. But, on the other hand, very small regions of both phases lead to increases in the interphase energy. As a result of the competition of these two factors, at carrier densities that are not very large, magnetoexcitonic droplets which contain several dozens of carriers should appear inside the nonmagnetic host. These carriers are locked inside the droplets and cannot move throughout the crystal.

But, on increase of the density of doped carriers, the portion of the excitonic phase increases, and its percolation begins—this is the concentration insulator-to-metal phase transition in a degenerate magnetoexcitonic semiconductor. Thus, magnetoexcitonic semiconductors should belong to a vast class of materials in which the charge-carrier-induced phase separation is possible (see the monograph [9] and the review article [10]).

These theoretical arguments may explain the unusual electric and magnetic properties of $La_{1-x}Sr_xCoO_3$ crystals first discovered in [11, 12]. Substitution of divalent Sr instead of trivalent La leads to the appearance of holes in the crystal. But it would be an error to think that all of the Sr ions act as acceptors. As is common for degenerate semiconductors, most

of the Sr atoms form clusters, whereas acceptors are only single Sr atoms not entering these clusters. For this reason the hole density should be considerably less than the number of Sr atoms in the crystal. It was found in [11, 12] that $La_{1-x}Sr_xCoO_3$ with $x > 0.05$ becomes ferromagnetic, and at $x = 0.2$ the insulator-to-metal transition takes place. But, according to [1], the region $0 < x < 0.18$ corresponds to the spin-glass regime. Possibly, this result does not contradict the scheme of magnetoexcitonic–nonmagnetic phase separation advanced here, since the mixture of the magnetically ordered excitonic regions and nonmagnetic ones may mimic the spin-glass behaviour of the sample.

2. Magnetoexcitons and holes

First, the magnetoexciton frequency for the insulating crystal should be determined. With this aim the exchange energy of the d shell with z electrons in it should be evaluated. If one assumes the same value of the d–d exchange integral A for all of the pairs of d electrons, one may write the Heisenberg Hamiltonian in the form

$$H_{dd} = -(A/2) \sum_{i \neq k}^{z} \sum_{i \neq k}^{z} (s_i \cdot s_k) = -(A/2) \left\{ \sum_{i=1}^{z} s_i \cdot \sum_{k=1}^{z} s_k - zs(s+1) \right\}$$
$$= -(A/2)\{S_t(S_t + 1) - zs(s+1)\} \tag{1}$$

where s_i is the spin operator for the ith electron, $s = 1/2$ its magnitude, and S_t the magnitude of the total spin of the d shell.

Using (1), one obtains the following expression for the exciton frequency corresponding to the transition $^1A_{1g} \rightarrow ^5T_{2g}$ ($z = 6$) at fixed ion positions:

$$\omega = 2\Delta - 3A \tag{2}$$

where Δ is the energy difference between t_{2g} and e_g orbital levels ($\hbar = 1$).

One should consider also the Jahn–Teller effect in the $^5T_{2g}$ state of the Co ion. In it, the state of four d electrons on the t_{2g} level is threefold degenerate, and deformation of the lattice should reduce the energy of this state. Obviously, this effect should be related mainly to the optical phonon branch as it corresponds to deformation of the elementary cell and not to displacement of the cell as a whole. For this reason the Hamiltonian of interaction of optical phonons with t_{2g} electrons may be represented in the form

$$H_i = (i/N^{1/2}) \sum_{fq} \sum_{\lambda\lambda'} \exp(iq \cdot f) v_{\lambda\lambda'}(q)(b_q - b_{-q}^*) a_{f\lambda}^* a_{f\lambda'} \tag{3}$$

$$v_{\lambda\lambda'}(q) = \exp(iq \cdot h) v_{\lambda\lambda'}(h) \tag{4}$$

where $a_{f\lambda}^*$ and $a_{f\lambda}$ are the t_{2g}-electron operators; f labels the elementary cells; and the index $\lambda = -1, 0, 1$ may be interpreted as the z-component of the pseudospin l of magnitude 1 labelling the degenerate levels (the true electron spin index is inessential here and for this reason is omitted). Furthermore, b_q^*, b_q are the operators for optical phonons with the wave vector q. For the sake of simplicity only one optical phonon branch is considered. N is the total number of elementary cells in the crystal.

Unfortunately, the information on the Hamiltonian of the electron–phonon interaction (equations (3) and (4)) is insufficient at present, and results obtained here on the Jahn–Teller effect are rather formal. The diagonal components of the interaction matrix may be presented in the form $v_{\lambda\lambda} = \lambda v$ ensuring the absence of the Jahn–Teller effect for completely filled subshells (cf. [13]) One may argue that the coefficients $v_{\lambda\lambda'}(h)$ represent electrostatic

multipole–multipole interactions and for this reason should vanish rapidly with increasing h. Thus, one may approximate these coefficients, putting in (4)

$$v_{\lambda\lambda'}(\boldsymbol{h}) = w_{\lambda\lambda'}d(\boldsymbol{h}, \boldsymbol{0}). \qquad (5)$$

Then, after diagonalizing the electron part of Hamiltonian (3),

$$\sum_{\lambda\lambda'} w_{\lambda\lambda'}a_{f\lambda}^*a_{f\lambda'} \rightarrow \sum_\mu \Lambda_\mu d_\mu^* d_\mu$$

where the d_μ are the new t_{2g} operators, one obtains

$$H_i = (\mathrm{i}/N^{1/2})\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{f})\Lambda_\mu(b_q - b_{-q}^*)d_{f\mu}^* d_{f\mu}. \qquad (6)$$

To find the gain in energy due to the Jahn–Teller effect caused by a magnetic exciton when the μth electron level is filled, one should write down the total phonon Hamiltonian and carry out the shift transformation of the phonon operators $b = \beta + \text{constant}$, eliminating terms linear in phonon operators:

$$H_{ph} = \nu\sum_q b_q^* b_q + (\mathrm{i}/N^{1/2})\sum_q\sum_\mu \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{f})\Lambda_\mu(b_q - b_{-q}^*)$$

$$= \nu\sum_q \beta_q^*\beta_q - \delta_\mu \qquad \delta_\mu = \Lambda_\mu^2/\nu. \qquad (7)$$

Here ν is the frequency of the relevant optical phonons, and δ is the Jahn–Teller gain in the energy. Obviously, it is at its maximum at the maximum Λ_μ, and in what follows only this value Λ will be treated. Then the magnetoexciton frequency, with allowance for the Jahn–Teller effect, should be given by $\omega_{JT} = \omega - \delta$ with ω given by (2). Hence, accounting for the Jahn–Teller effect is tantamount to renormalization of the magnetoexcitonic frequency.

Now we turn to considering holes. First we consider a hole in the nonmagnetic phase, assuming that holes are located on Co ions, too. This leads to the appearance of a fivefold-occupied t_{2g} level among the sixfold-occupied ones. The hole may move over the crystal, as the hopping integral t between neighbouring atoms is nonzero. But for d levels the strong inequality $A \gg t$ should hold, as A is of zeroth order and t of first order in the small orbital overlap for neighbouring atoms. For this reason one can ignore this motion in the zeroth approximation, and, according to (1), in the first approximation the hole energy reckoned from the energy of the crystal in the nonmagnetic state is given by

$$E_h(1/2, \boldsymbol{k}) = -3A/4 - 6t\gamma_k$$
$$\gamma_k = [\cos(k_x a) + \cos(k_y a) + \cos(k_z a)]/3 \qquad (8)$$

($\boldsymbol{k}$ is the hole quasimomentum; the lattice of magnetic ions is assumed to be simple cubic with the lattice constant a).

Let us assume now that the entire crystal is in the ferromagnetically ordered magneto-excitonic state and contains a hole. One should consider two possible hole states.

(1) The hole corresponds to the spin-3/2 state ($t_{2g}^4 e_g$) of the magnetic ion, and then its energy reckoned from the energy of the crystal in the ferromagnetic state is

$$E_h(3/2, \boldsymbol{k}) = 3A/4 - \Delta - 6t'\gamma_k \qquad (9)$$

where t' is the hopping integral for e_g orbitals.

(2) The hole corresponds to the spin-5/2 state ($t_{2g}^3 e_g^2$). In this case the hole energy is

$$E_h(5/2, \boldsymbol{k}) = -7A/4 - 6t\gamma_k. \qquad (10)$$

One obtains from (2), (9), and (10) in the zeroth approximation in t for the difference between these energies

$$E_h(5/2) - E_h(3/2) = \Delta - 5A/2 = -A + \omega/2. \tag{11}$$

According to (11), at the small exciton frequencies $\omega \ll A$ in which we are interested, the hole spin-5/2 state is more energetically favoured than the spin-3/2 state. Thus, only the former will be treated. Using (8) and (10), one finds the difference between hole energies in nonmagnetic and magnetic states:

$$U = E_h(1/2) - E_h(5/2) = A. \tag{12}$$

Thus, according to (12), the energy of a system with one hole is lower by the quantity U in the ferromagnetic state than in the nonmagnetic state. In the zeroth approximation in t, this result is valid for any magnetic ordered or disordered state of the crystal.

3. Single-hole magnetoexcitonic complexes

Let us consider now the ground state of the hole. As was already pointed out, it should be the self-trapped state. It may described by a theory obtained as a generalization of earlier theory [6, 7]. Two limiting cases will be discussed: $6t \ll \omega_{JT}$ and $6t \gg \omega_{JT}$. In both of these cases the inequality $A \gg \omega_{JT}$ will be assumed.

In the first case only one magnetic exciton is created. The energy of such a system is found from the well known Lifshitz equation [14]

$$1 + (U/N) \sum_k (E - \omega_{JT} - 6t\gamma_k)^{-1} = 0 \tag{13}$$

which gives

$$E = -U + \omega_{JT} - 6t^2/U. \tag{14}$$

The second case is many excitonic. It is assumed that each d shell inside a sphere of a radius R is excited into the ${}^5T_{2g}$ state. The hole is localized inside this region, whose radius should be determined from the condition of the minimum total energy of the system.

One should take into account that if two neighbouring ions are excited, an exchange interaction between them arises. If this exchange is ferromagnetic, then, certainly, ferromagnetic ordering should be established inside the magnetoexcitonic complex. But if it is antiferromagnetic, the ordering of the complex may be not only ferromagnetic but also collinear or canted antiferromagnetic.

To simplify the calculations we shall assume that the lowest Jahn– Teller component is nondegenerate. Then for hole hoppings a theory developed in [7, 15] may be applied. This theory is valid for $A \gg t$ and takes into account that in the zeroth approximation in t/A the spin of the carrier is bound rigidly to the spin of the atom at which it is located at the moment. After transition to a neighbouring atom, the carrier spin is bound to its spin. For this reason the effective hopping integral t_e for a carrier depends on the angle 2θ between regular directions of spins in the magnetic structure which is assumed to be canted antiferromagnetic and, hence, as limiting cases includes both collinear ferromagnetic and antiferromagnetic structures:

$$t_e = t[\cos^2 \theta + (2S + 1)^{-1} \sin^2 \theta]^{1/2}. \tag{15}$$

Here S is the spin magnitude for the carrier-free magnetic atom, which is equal to 2 in the case of the state ${}^5T_{2g}$.

The carrier band bottom lies at $-6t_e$. As seen from (15), the effective hopping integral for the ferromagnetic ordering is $5^{1/2}$ times larger than for the antiferromagnetic one. For this reason the carrier hopping tends to establish the ferromagnetic ordering. But as was assumed above, the direct exchange between excitons tends to establish antiferromagnetic ordering. Hence, depending on the parameters of the system, the minimum of the energy of the system may be attained for both of these magnetic structures inside the excitonic complex, as well as for the noncollinear antiferromagnetic structure. Other structures seem to be less preferable.

It is natural to assume that the many-excitonic complex occupies a region of radius R. For $R \gg a$, where a is the lattice constant, the effective-mass approximation is valid for the hole. Then the total energy of the system is given by the expression

$$E = -U - 6t_e + k^2/2m + (4\pi/3)D(R/a)^3 \tag{16}$$

where U is given by (12), the hole effective mass m is related to the hopping integral by $1/2m = t_e(\theta)a^2$, and D is the energy spent in creation of the excitonic phase per atom:

$$D = \omega_{JT} - K\cos 2\theta \qquad K = 3IS^2 \qquad (I < 0) \tag{17}$$

where I stands for the interexcitonic exchange integral.

The parameter k in (16) should be determined from conditions on the boundary between the nonmagnetic and excitonic phases. For A and R large enough, when the hole attenuation length outside the excitonic phase is small compared to R, one may put $k = \pi/R$.

Equations (16) and (17) resemble the corresponding equations in the theory of electron self-trapping in an antiferromagnetic semiconductor [6, 7]. But, unlike in them, the energy is here minimized not only with respect to R but also with respect to θ.

First, let us consider the collinear structures. Then, in full analogy with [6, 7], after minimizing E (16) with respect to R the following expressions are obtained:

$$E = -U - 6t_e + (5\pi^{8/3}/3)t_e^{3/5}(2D)^{2/5} \tag{18}$$

$$R = a(\pi t_e/2D)^{1/5}. \tag{19}$$

As follows from (15) and (18), the antiferromagnetic exciton ordering is more energetically favoured than the ferromagnetic, if

$$t/\omega_{JT} \leqslant 34, 9[(1 - \kappa)^{2/5} - 0.62(1 + \kappa)^{2/5}]^{5/2} \tag{20}$$

with $\kappa = K/\omega_{JT} < 0$. As follows from (20), for $\kappa \in [-1, 0]$ condition (20) is compatible with the condition $t \gg \omega_{JT}$ under which (20) was deduced.

The energies of the canted structures may turn out to be still lower than the energies of the collinear states (18). By minimizing (16) with respect to both R and θ, one obtains the following equation for determination of the canting angle:

$$3t^2\{-6 + \pi^2[2D(\theta)/\pi t_e(\theta)]^{2/5}\} = 20\pi Kt_e(\theta)[\pi t_e(\theta)/2D(\theta)]^{3/5}. \tag{21}$$

The equilibrium radius dependence on the canting angle is described by equation (19) in which both t_e and D are assumed to be dependent on θ. It is worth mentioning that, despite a very high gain in the energy due to the self-trapping ($\sim A$) the radius of the excitonic complex does not include the large parameter A and in typical cases may amount only to a few lattice constants.

As an example, one may evaluate the range inside which the canted structure is more energetically favoured than the collinear structures, taking $K = -\omega_{JT}/2$. Then one obtains from (21) that this takes place in the range of values of t/ω_{JT} between 8.9 and 21.5. At lower values the collinear antiferromagnetic state should be stable and at higher values the ferromagnetic should be stable.

4. Magnetoexcitonic phase separation in degenerate semiconductors

In degenerate semiconductors with large hole density, the magnetoexcitonic self-trapping of holes should occur in a correlated manner as the holes interact with each other. One might expect that it will be energetically favoured for a magnetoexcitonic region to capture not one but several holes simultaneously as the energy expenditures for creation of a common magnetoexcitonic region are less that those for creation of a separate magnetoexcitonic region for each hole.
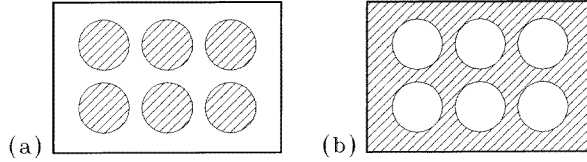

Figure 1. Two-phase states of a degenerate semiconductor: (a) insulating; (b) conducting. The magnetoexcitonic part of the crystal is shaded, while the nonmagnetic part is not.

But this factor competes with other factors hindering the hole concentration. Here we shall consider the case where the impurity diffusion is negligible, so that ionized acceptors and, hence, their charge, remain distributed uniformly over the crystal. This means that the hole concentration in some regions of the crystal leads to the appearance of Coulomb forces, increasing the energy. On the other hand, the concentration of holes increases their kinetic energy. For this reason the optimum distribution of magnetoexcitonic regions and holes arising as a result of competition between above-mentioned factors should be found.

The calculation presented below is performed as a generalization of calculation carried out in [7, 8]. A variational method is used. The trial wave function of the system is chosen in the following way. Two different geometries of the two-phase state are considered: (1) the insulating state when the holes are concentrated inside magnetoexcitonic regions assumed to be spherical droplets which are separated from each other by the insulating nonmagnetic phase, i.e., the region of the excitonic phase is multiply connected (figure 1(a)); and (2) the highly conducting state when the excitonic region over which holes may move freely is simply connected. The magnetoexcitonic phase is the host for the droplets of the insulating nonmagnetic phase (figure 1(b)).

The magnetic ordering in the magnetoexcitonic phase may be collinear ferromagnetic or antiferromagnetic, or indeed canted antiferromagnetic. The latter may be stable as the indirect exchange via charge carriers in the case considered cannot be described by the RKKY theory, as its applicability condition $\mu \gg AS$ is not met (μ is the Fermi energy). In reality, this inequality is replaced by the opposite one, which means that the indirect exchange cannot be described in terms of an effective Heisenberg Hamiltonian, which, certainly, cannot allow the canted two-sublattice ordering. But for an isotropic non-Heisenberg exchange, such ordering is possible [16].

The variational parameters for the ground-state energy of the system are the ratio x of volumes of the nonmagnetic and magnetoexcitonic regions, the radius R of the spherical droplets of the minority phase inside the host, and the canting angle 2θ for antiferromagnetic sublattice moments in the magnetoexcitonic phase. Hence, an additional variational parameter θ appears here as compared to [7, 8].

The total energy of the system is given by the equation

$$E = E_V + E_S + E_C + E_M. \tag{22}$$

Here E_V and E_S are respectively the bulk and surface energies of the degenerate electron (or hole) gas confined inside the magnetoexcitonic phase which is calculated in the Born–Oppenheimer approximation. With allowance for (15) one may generalize the corresponding equations of [7, 8] by taking into account the dependence on canting angle of the conduction band bottom and that of the hole effective mass. Thus, one may write these equations per volume unit:

$$E_V = -6t_e n + (3/5)\mu_p n(1+x)^{2/3} \tag{23}$$

$$E_S = (3/16)(\pi/6)^{1/3}\mu_p n^{2/3} R^{-1}\beta(1+x)^{1/3} \tag{24}$$

$$\mu_p = (6\pi^2 n)^{2/3}/2m = t_e(6\pi^2 na^3)$$

where n is the average hole density, t_e is determined by (15) with $S = 2, \beta = 3$ for the geometry of figure 1(a) and $\beta = 3x$ for the geometry of figure 1(b).

The quantity E_C in (22) denotes the Coulomb energy arising due to the nonuniform distribution of the holes over the crystal. It is found by dividing the crystal into Wigner–Seitz cells where each charged droplet of the minority phase is surrounded by a spherical layer with charge equal in value but opposite in sign. In full accordance with [7, 8], one may write in the jellium model

$$E_C = (2\pi/5)(e^2/\varepsilon_0)n^2 R^2 f(x) \tag{25}$$

where e is the electron charge, ε_0 is the dielectric constant of the crystal, and

$$f(x) = \begin{cases} 2x + 3 - 3(1+x)^{2/3} & \text{for the case of figure 1(a)} \\ x[3x + 2 - 3x^{1/3}(1+x)^{2/3}] & \text{for the case of figure 1(b).} \end{cases}$$

Finally, the quantity E_M entering (22) is the density of the exchange energy of the magnetic subsystem. With allowance for (12) and (17) it is written in the form

$$E_M = -Un + D/[(1+x)a^3]. \tag{26}$$

One concludes from (23)–(26) that only the surface energy increasing with diminishing R and the Coulomb energy decreasing with diminishing R depend on R. This makes it possible to carry out minimization of the sum $Q = E_S + E_C$ at fixed x and θ in an explicit form, which leads to the following equations for the stationary values:

$$Q = E_S + E_C = 0.579\gamma n\beta[f(x)/\beta]^{1/3}(1+x)^{2/9}$$

$$\gamma = (\mu_p^2 n^{1/3}e^2/\varepsilon_0)^{1/3} \tag{27}$$

$$nR^3 = 0.0601\mu_p\beta(1+x)^{1/3}\varepsilon_0/[f(x)e^2 n^{1/3}].$$

After substitution of (27) into (22) a numerical minimization of the total energy with respect to x and θ is required.

In carrying it out one should keep in mind that there are two different branches of the total energy E_a or E_b corresponding to the two geometries of figures 1(a) or 1(b), as they differ in the equations for Q (27) due to the difference in their values of $f(x)$ and β. A numerical analysis shows that, at the same values of the canting angle θ, the quantity E_a is less than E_b for all $x > 1$. For all $x < 1$ the relationship between them changes to the opposite one. This means that for $x > 1$ the minimum total energy (22) is reached for the geometry of figure 1(a) and for $x < 1$ for the geometry of figure 1(b).

One can easily see from (22), (23), (26) and (27) that with the hole density n fixed, the parameters of the two-phase state are uniquely determined by the following set of dimensionless quantities: $\nu = na^3, \kappa = K/\omega_{JT}, \tau = t/\omega_{JT}$ and $\xi = e^2/(\varepsilon_0 a\omega_{JT})$. The numerical calculations were carried out for the following values: $\tau = 10$ and $\xi = 5$.

The results may be summarized as follows. For a rather weak antiferromagnetic exchange $\kappa = -0.5$ the magnetoexcitonic phase exists and has collinear ferromagnetic structure ($\theta = 0$) for any hole densities. One might think that the ferromagnetic structure contradicts the results indicated at the end of the section 3 which are obtained for the same κ-value, but one should keep in mind that the problems treated in section 3 and here are not equivalent: the former is single hole and the latter many hole. This is reflected by the fact that in latter case the additional parameter ξ describing the Coulomb interaction should be introduced. For this reason the results just mentioned are compatible.

The transition from the two-phase insulating state (figure 1(a)) to the two-phase highly conducting state (percolation of the holes and magnetic excitons) occurs with increasingly reduced hole density at the value $\nu_p = 0.036$. This concentration transition was found to be first order: it is accompanied with an abrupt change of the optimal values of the variational parameters: x changes from the value $x_a = 1.07$ to $x_b = 0.93$, and R from $R_a = 6.21a$ to $R_b = 6.30a$. The number of holes in the magnetoexcitonic droplet at the percolation density $N_a = (4\pi/3)(R_a/a)^3\nu_p(1 + x_a)$ is 75.

On the other hand, as the jump in the parameter values at the percolation is rather small, one might suspect that the abrupt transition is an artifact following from the circumstance that both of the geometries of figure 1 fail to reproduce the real geometry of the two-phase state close to the percolation density. In reality, the percolation possibly occurs via the second-order phase transition.

For a stronger antiferromagnetic exchange $\kappa = -0.7$ (and the same values $\tau = 10$ and $\xi = 5$) the magnetoexcitonic part of the crystal has canted antiferromagnetic structure. The percolation of the conducting magnetoexcitonic phase which takes place at $\nu_p = 0.030$ is accompanied by jumps not only of the quantities x and R but also by a jump of the canting angle. In this case jumps of the parameters at the percolation densities are more pronounced: $x_a = 1.17 \rightarrow x_b = 0.87$; $R_a = 5.60a \rightarrow R_b = 5.64a$; $2q_a = 97° \rightarrow 2\theta_b = 111°$. The number of holes in a magnetoexcitonic droplet close to the percolation density is 48.

Further increase in the antiferromagnetic exchange integral up to $\kappa = -0.9$ leads to collinear antiferromagnetic ordering in the region of existence of the two-phase state. The percolation parameters are as follows: $\nu_p = 0.010$, $x_a = 1.10 \rightarrow x_b = 0.93$, $R_a = 6.22a \rightarrow R_b = 6.40a$, and the number of the holes in a droplet is 21.

Now we discuss qualitatively the effect of an external magnetic field on the phase separation and resistivity of the two-phase systems. As follows from energetic considerations, the field tends to increase the volume of the magnetic phase. In particular, if at zero field the system is in the insulating two-phase state but close to percolation, the applied field may cause percolation, i.e., an insulator-to-metal transition which is equivalent to a giant negative magnetoresistance. In addition, like in other spontaneously magnetized degenerate semiconductors, negative magnetoresistance related to magnetoimpurity capture and scattering of charge carriers [7] may be realized in the highly conducting state of the materials considered. The negative magnetoresistance in such a state of $La_{1-x}Sr_xCoO_3$ was observed in [17].

In the calculations presented above, the magnetoexciton frequency was considered to be density independent. But, in reality, one should also take into account the fact that doping changes the lattice constant of the crystal and, hence, the crystalline field. For this reason the magnetoexciton frequency should depend on the degree of doping. In [2] it was even assumed that doping of the initial material with Sr stabilizes the high-spin state of the Co ions via this mechanism and not via the exciton–hole interaction. But in reality the sign of the effect caused by the lattice expansion on doping is unclear—it may be just the opposite. At present, it is impossible to decide which of these mechanisms is more powerful:

they may work simultaneously. Taking into account the doping dependence of the exciton frequency in the phase-separation calculation will be reasonable only after obtaining reliable experimental data on this effect.

5. Conclusions

States of charge carriers in transition metal compounds with low-frequency zero-spin–nonzero-spin transitions (e.g. some Co compounds) have been investigated. Magnetoexcitonic self-trapping of carriers (holes) is possible in these compounds when a complex consisting of a hole and one or several magnetic excitons arises. The energy spent in magnetoexciton creation (the transition of the ion into a magnetic state) is compensated by the gain in energy due to the exchange between the hole and magnetoexcitons. In the ground state of degenerate semiconductors, spontaneous separation into magnetic and nonmagnetic phases is possible with all of the holes concentrated inside the former.

Depending on the direct exchange between excitons, collinear ferro- and antiferromagnetic orderings, as well as canted antiferromagnetic ordering, are possible in the systems under consideration. At relatively low hole densities the magnetic phase is a set of small droplets inside the nonmagnetic host. On increase of the density, percolation of holes and magnetic excitons takes place, which leads to the transition from the insulating phase-separated state to the highly conducting phase-separated state.

Acknowledgments

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