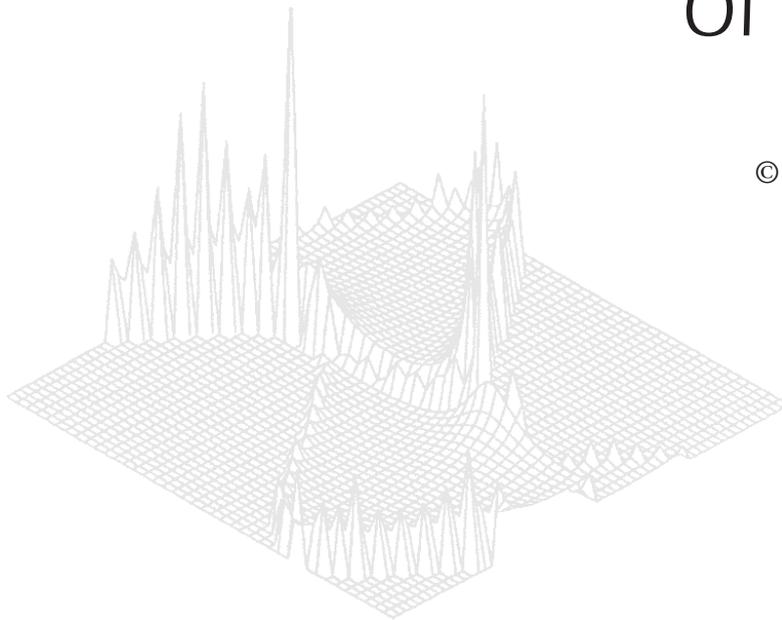

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Magnetoimpurity Theory of Manganites and Other Colossal Magnetoresistance Materials*

E. L. Nagaev

Institute for High Pressure Physics of RAS, Troitsk,
Moscow Region, 142092, Russia.
tsir@elch.chem.msu.ru

Abstract

A critical review is given of the physics of colossal magnetoresistance (CMR) materials (manganites and other degenerate ferromagnetic semiconductors). The basic idea is that their specific properties (the resistivity peak close to T_C , CMR and so on) are not related to the electron–lattice interaction but are caused by static fluctuations of the magnetisation induced by ionised donors or acceptors. Their screening by charge carriers causes fluctuations of their density and, hence, fluctuations of the intensity of indirect exchange via them. The fluctuations of the magnetisation induced by the latter are maximally close to T_C , which explains the specific features of these materials.

1. Manganites as Ferromagnetic Semiconductors

A specific feature of the ferromagnetic semiconductors is a peak of the resistivity ρ close to the Curie point T_C . The ρ peak is suppressed by an external magnetic field which leads to negative isotropic colossal magnetoresistance (CMR). These correlated properties are common for all the ferromagnetic semiconductors, both the degenerate and nondegenerate ones and independently of the charge carrier sign, and their number amounts to several tens. It manifests itself also in the initially antiferromagnetic semiconductors if, as a result of their doping, they convert into the ferromagnetic semiconductors (Nagaev 1982).

At present, of special interest to investigators are the ferromagnetic semiconductors $\text{La}_{1-x}\text{Di}_x\text{MnO}_{3+y}$, obtained from the antiferromagnetic insulator LaMnO_3 by doping with the divalent ions $\text{Di} = \text{Ca}, \text{Sr}$ and so on, or by introducing excess oxygen. Both Di and excess oxygen inject holes in the crystal. One would be wrong in assuming that this interest is related to the fact that the ρ peak and CMR are pronounced especially strongly in manganites. On the contrary, these effects are much weaker than in many other ferromagnetic semiconductors. But in the manganites, unlike other ferromagnetic semiconductors, the CMR peak is achieved at room temperatures, which makes them especially promising for practical applications.

Many physicists engaged in investigations of the manganites ignore the fact that, qualitatively, the properties of the manganites with complete ferromagnetic

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ordering are quite similar to those of other ferromagnetic semiconductors. First of all, the manganites are really degenerate ferromagnetic semiconductors, at least at $0.2 < x < 0.3$ or $0.1 < y < 0.3$, though some authors believe that they are metals. Really, one can consider a conductor as a degenerate semiconductor if the number ν of holes per atom over which they move is small compared with 1. Experimental data on the location of the holes in manganites are contradictory: most authors believe that they move over Mn ions, but there is experimental evidence that, in actual reality, they move over the O ions (see Nagaev 1996a). If this is the case then the conditions for the inequality $\nu \ll 1$ are still more favourable as the number of the O ions is three times larger than the number of Mn ions. It is clear that ν should be less than x or y as the impurity atoms can form clusters. The impurities entering the clusters are not electroactive. Only separate impurity atoms can function as acceptors, but nobody can tell how many impurity atoms are separate. As is well known, in degenerate semiconductors the number of donors or acceptors can be several orders of magnitude less than the total number of impurity atoms. But, even if one assumes the worst case for degenerate semiconductors, i.e. $\nu = x$, nevertheless, the results obtained for degenerate semiconductors remain in force, at least, semiquantitatively, up to $x = 0.3$.

The possibility of considering manganites with x up to 0.3 as degenerate semiconductors is confirmed experimentally by the identification of the giant redshift of the optical absorption edge occurring with decreasing temperature (Loshkaryeva *et al.* 1997). Such a shift is the most pronounced specific feature of the ferromagnetic semiconductors and is observed in all of them without exception (Nagaev 1983). Another experimental confirmation that the number of holes in ferromagnetic highly-conductive manganites is relatively small is the fact that the material with $x = 0$ and $y = 0.11$ belongs to them (Troyanchuk and Patushonok 1989; Krinchik *et al.* 1991).

Usually the properties of the magnetic semiconductors are described within the framework of the sd model in which the term ‘d-electrons’ is used for the localised electrons of partially filled electronic d- or f-shells, and the term ‘s-electron’ for mobile conduction electrons and holes. Between them the sd exchange interaction exists with intensity AS , where A is the exchange integral between a d-spin and charge carrier and S is the d-spin magnitude. Classification of the magnetic semiconductors is carried out by comparison of the s-energy bandwidth W with AS .

The not very transparent term ‘double exchange’, introduced by Anderson and Hasegawa (1955), refers to the usual exchange interaction between the charge carrier and localised spin, when it is so strong that its energy exceeds the carrier energy band width ($W \ll AS$). Physically, such a situation is realised in the transition metal compounds, if the electrons or holes move over their partially filled d-levels. For example, in the manganites it should occur if the holes move over the Mn^{3+} ions, converting each of them in the Mn^{4+} ion when dwelling at it. There is experimental evidence in favour of this scenario, but there is other evidence in favour of the opposite scenario too. In the latter case the holes move over the O^{2-} ions, and then the opposite inequality $W \gg AS$ should be met (see e.g. Nagaev 1996a). Thus, the problem of double exchange in manganites is not solved conclusively yet.

But double exchange is, certainly, absent from the rare-earth compounds where the electrons move, not over the partially filled f-shells, but over the empty s- or d-shells. Under typical conditions, in the rare-earth metals and their compounds, W exceeds AS by an order of magnitude. For example, in EuO W amounts to 4 eV, and AS only to 0.25 eV (Nagaev 1983).

It was assumed in Millis *et al.* (1995) that a necessary condition for the resistivity peak and CMR is double exchange. This assumption is certainly wrong: these specific features are general for all ferromagnetic semiconductors. For example, EuO with $W \gg AS$ displays the highest resistivity peak among all ferromagnetic semiconductors, a variation which amounts to 19 orders of magnitude (see Nagaev 1983).

Similar properties are displayed by tens of other ferromagnetic semiconductors without double exchange, in particular, EuS, NdCr₂Se₄, NdCr₂S₄ and so on (Nagaev 1983). Hence, one cannot consider the double exchange as a necessary condition for the resistivity peak and related CMR. But one can state that both these features manifest themselves at any strength of the exchange interaction between the charge carriers and localised spins.

2. Role of the Jahn–Teller Effect and Mechanisms of the Isotope Effect

Many physicists try to relate the resistivity peak and CMR in the manganites to the presence of the Jahn–Teller (JT) Mn³⁺ ions in them (the vital importance of the JT effect for the specific properties of manganites was expressed by Millis *et al.* 1995). But there are numerous experimental arguments providing evidence for a subordinate role for the JT effect. As already mentioned, the resistivity peak and CMR are universal properties of ferromagnetic semiconductors. In my book (Nagaev 1983) a list of 30 ferromagnetic semiconductors is presented with such specific properties. However, none of them is a JT system, except for the manganites. In other words, the vast majority of systems with the same magnetic and electric behaviour as manganites are the non-JT ones and, hence, it is impossible to ascribe their specific properties to the JT effect.

Moreover, the effects considered manifest themselves in non-JT systems far stronger than in the JT systems. For example, as already mentioned, the height of the resistivity peak in the non-JT EuO amounts to 19 orders of magnitude, and in EuS to 7 orders (Nagaev 1983), whereas in the JT La–Mn–O manganites only to 2 orders (van Santen and Jonker 1950; Urushibara *et al.* 1995). If the resistivity peak of the JT materials had been considerably higher than that of the non-JT materials, possibly there would have been a necessity to invoke the JT phonons to explain this enhanced effect. But, in reality, the situation is quite opposite. Lightheartedly, one can even assume that the JT effect hinders the resistivity peak and CMR. But seriously, I believe that the JT effect enhances, to some extent, the total resistivity of the CMR materials but is not responsible for their specific features.

At last, judging from experimental data on the La–Mn–O system (Urushibara *et al.* 1995), lattice phase transitions in manganites are only accompanied by small changes in resistivity which does not provide evidence for an anomalously strong hole–lattice coupling. Nevertheless, in some cases there are experimental data providing evidence for changes in the lattice at temperatures close to T_C (see Millis 1998). However, these changes cannot be the origin, but rather a

consequence of the existence of this peak and of the corresponding changes in the hole states. As for the peak itself, it can be caused by a quite different reason.

It is instructive to note that the standard magnetic order–disorder phase transition is also accompanied by a change in the lattice state, but nobody has tried to consider the magnetostriction as the origin of the phase transition. One considers it as a phenomenon accompanying the phase transition caused by a purely magnetic origin.

Much more nontrivial is the problem of the giant isotope effect observed in some manganites. Replacement of ^{16}O by ^{18}O leads to a considerable lowering of the Curie point transition (Zhao *et al.* 1996; Isaak and Frank 1998) from the highly-conductive state to the insulating state (Zhao *et al.* 1997; Babushkina *et al.* 1998*a*, 1998*b*; Zhou and Goodenough 1998) and a change in the structure of the magnetically unsaturated state (Ibarra *et al.* 1998). Beginning with the BCS superconductors, many physicists have been accustomed to relate the isotope effect to electron–phonon coupling. If one accepts the electron–phonon mechanism for the isotope effect, one should accept an anomalously strong hole–phonon coupling in manganites (Zhao *et al.* 1996), or special almost-resonance conditions when a normal hole–phonon coupling leads to dramatic changes in the behaviour of the system (Kresin and Wolf 1997; Babushkina *et al.* 1998*a*, 1998*b*).

However, in Nagaev (1998*a*, 1998*b*) it was shown that non-electron–phonon mechanisms for the isotope effect exist. They cannot be realised in the BCS superconductors but are inherent in the oxide compounds, including manganites. As an example of a mechanism for the isotope effect not related to hole–phonon coupling, an isotope dependence of the number of excess or deficient oxygen atoms at thermodynamic equilibrium is proposed.

It is assumed that thermodynamic equilibrium is established at the temperature of sample preparation, so that the chemical potentials of oxygen in the crystal and in the surrounding atmosphere are equal. But the former depends on the number of excess or deficient atoms in the crystal, and the latter on the oxygen atom mass via the translational and rotational energies, as well as the dissociation energy for the oxygen molecule. As the number of oxygen imperfections remains frozen at lower temperatures, this dependence should lead to an isotope dependence of the equilibrium charge carrier density and volume of the lattice.

As the excess or deficient oxygen atoms are acceptors or donors, respectively, it implies an isotope dependence of the hole density, which manifests itself in the electro-conductivity and in the intensity of the indirect exchange via holes. Actually, estimates carried out (Nagaev 1998*a*, 1998*b*) show that the number of holes in the ^{18}O -replaced samples can exceed that in the ^{16}O -based samples by up to 30%. Certainly, such a mechanism is not universal: it manifests itself only if the contribution of the nonstoichiometric oxygen to the total number of holes is comparable or exceeds that of the Di ions.

Another mechanism for the oxygen nonstoichiometry relies on the fact that the difference in the number of nonstoichiometric oxygen atoms must lead to a difference in the volumes for samples with different isotopes. This difference corresponds to an effective pressure of a few kbar. But the metal–insulator transitions in manganites are strongly pressure-dependent (Zhao *et al.* 1997; Zhou and Goodenough 1998; Ibarra *et al.* 1998) and thus this effective pressure can be sufficient to cause such a transition.

It is very important to note that an experimental investigation of the giant isotope effect (Frank *et al.* 1998) confirmed that the effect is related to the oxygen excess in the manganite in accordance with the mechanism (Nagaev 1998*a*, 1998*b*). The disappearance of the excess oxygen diminishes the isotope effect drastically.

3. Magnetopurity Mechanism for the Colossal Magnetoresistance Materials

Now we discuss the real mechanism for the appearance of the resistivity peak and CMR in ferromagnets. First of all, it should be mentioned that the resistivity peak of ferromagnetic conductors is necessarily related to the imperfections of the crystal lattice. For example, in perfect Ni crystals at the Curie point only a break in the resistivity versus temperature curve is observed, and only the temperature derivative of the resistivity is peaked. But if one makes the same crystal imperfect in some manner, then it will display the resistivity peak in the vicinity of the Curie point. In degenerate magnetic semiconductors the part of imperfections is played by the ionised donor or acceptor impurity.

Along with this, there is no question that the magnetic state of the crystal influences the charge transport. In the theory, given below and called the magnetopurity theory (Nagaev 1983; Shklovskii and Efros 1979), both these factors are united in the following manner. For an increase in temperature, the nonmagnetic impurity atoms acquire effective magnetic moments which increase the interaction of charge carriers with impurity atoms. These effective moments are maximal in the vicinity of T_C , and there the resistivity of the crystal is maximal.

In more detail, in the degenerate semiconductors, both magnetic and nonmagnetic, the donor electrons (or the acceptor holes) are delocalised, and the donors are ionised. But the delocalised electrons continue to interact with randomly located ionised donors. This randomness causes two main effects: a part of the charge carriers goes over to the localised states, but they are localised not at separated donors but on their groups arising as a result of the impurity density fluctuations. One refers to these as the carriers in the band-tail states. Those carriers which have higher energies are delocalised but they are scattered by the impurity, which leads to their finite mobility. In addition, they screen the electrostatic field of the ionised impurity which results in an enhanced density in the vicinity of the impurity atoms.

The peculiarities of degenerate ferromagnetic semiconductors are determined by the fact that the charge carriers tend to support the ferromagnetic ordering in them, as the latter ensures their minimal energy (Nagaev 1983). With increasing temperature the ferromagnetic ordering in the crystal is destroyed. But its destruction in the vicinity of the impurities occurs more slowly than in the rest of the crystal, as in this vicinity the density of charge carriers is higher. Hence, the degree of the ferromagnetic order is also higher there. For this reason an excessive magnetic moment arises close to the impurities, for an increase in temperature.

The charge carrier scattering by this excessive moment is combined with its scattering by the screened Coulomb potential. Hence, the total scattering increases with temperature. Correspondingly, the scattering of the delocalised electrons and the number of electrons localised in the band-tail increases also. The resistivity grows and it can even happen that, due to the increased attraction

of the electrons to donors, these electrons will be completely localised at them, i.e. the Mott transition to the insulating state will take place.

For a further increase in temperature, the excessive magnetisation close to the impurities becomes destroyed, too, and the crystal becomes highly conductive again. The same occurs in a magnetic field, which tends to establish complete ferromagnetic ordering everywhere and, hence, diminishes the difference in the magnetisation close to and far from the impurities. This is just the origin of CMR.

An analysis of the interaction of the charge carriers with the impurity is carried out with the use of the condition of the constant electrochemical potential and the Poisson equation. The difference from the standard approach to nonmagnetic systems is the fact that the dependence of the electron energy on magnetisation is taken into account. In the Born–Oppenheimer approximation, it is assumed that the magnetisation $M(r) = M(n(r))$ is a smooth function of coordinates because the typical length for its change, i.e. the screening length, is large in semiconductors (Shklovskii and Efros 1979). For this reason, for example, at $W \gg AS$ in the spin-wave approximation the corresponding contribution to the electron energy is equal to $-AM(n(r))/2$, if the conduction electrons are completely spin-polarised.

As a result, one finds that the total interaction of the conduction electron with the electrostatic field of the ionised donor and the excess magnetisation in its vicinity is given by the screened Coulomb-like potential, in which the true electron charge e is replaced by the effective charge $e_{\text{eff}} = e(\epsilon/\zeta)^{1/2}$, exceeding the former. The effective dielectric constant ζ is related to the true dielectric constant ϵ by $\zeta = \epsilon(1 - \Gamma)$, where at $W \gg AS$ the magnetoelectric constant G which accounts for the dependence of the local magnetic ordering on the electron density is given by (Nagaev 1983, 1996a, 1996b, 1997b)

$$\begin{aligned} \Gamma &= \frac{A}{2} \frac{dM}{dn} \frac{dn}{d\mu} \sim \frac{A^2 T}{(H + T_C/S)^2} \frac{d\nu}{d\mu} \quad \text{for } T_C/S \ll T \ll T_C, \\ \Gamma &\sim \frac{A^4 S^2 (S+1)^2 m a^3 k_F \nu}{\mu^2 T} \quad \text{for } T \gg T_C, \quad H = 0 \quad (\nu = n a^3), \\ \Gamma &\sim \frac{A^2}{T} \frac{d\nu}{d\mu} \exp\left(-\frac{(H + A\nu/2)S}{T}\right) \quad \text{for } T \gg T_C, \quad H \rightarrow \infty, \end{aligned} \quad (1)$$

where n is the electron density, μ the Fermi energy and a the lattice constant. In the opposite limiting case of double exchange, $W \ll AS$, an explicit expression for the magnetoelectric constant was obtained only for the spin-wave region (Nagaev 1983, 1996a, 1996c):

$$\Gamma \sim \frac{n^{1/3} a t T}{S^2 (H + T_C/S)^2}, \quad (2)$$

where t is the electron hopping integral.

As seen from (1) and (2), for an increase in temperature, the effective charge e_{eff} of an impurity atom increases in the spin-wave region and decreases in

the paramagnetic region. Thus, it is maximal in the vicinity of T_C , where the resistivity maximum should be located. The magnetic field decreases e_{eff} , making it approach e .

At relatively small changes in ρ , using an expression for the density of states in the band-tail presented by Shklovskii and Efros (1979), and replacing e by e_{eff} , one obtains for the total number of electrons localised in the tail:

$$n_t \sim \left(\frac{me^2 n^{1/2} r_s^{1/2}}{\zeta} \right)^{3/2}; \quad r_s = \sqrt{\frac{\zeta}{\epsilon}} r_s^0; \quad \frac{1}{r_s^0} = \sqrt{\frac{4\pi e^2}{\epsilon} \frac{dn}{d\mu}}, \quad (3)$$

where m is the conduction electron effective mass. According to (3), $n_t \sim e_{\text{eff}}^{9/4}$, i.e. the number of electrons localised in the tail is maximal, and the number of delocalised electrons is minimal at the temperature at which e_{eff} is maximal.

Similarly, at this temperature the relaxation time is minimal for the scattering of delocalised electrons by the impurity. It is seen from the Brooks–Herring expression for scattering of conduction electrons by ionised impurities modified in the same manner as (3):

$$\tau_k^{-1} \sim \frac{e^4 n m}{k^3 \zeta^2} \left(\ln(1 + \eta) - \frac{\eta}{1 + \eta} \right); \quad \eta = 4k^2 r_s^2. \quad (4)$$

As for semiconductors $\eta \gg 1$, the relaxation time is proportional to $1/(e_{\text{eff}}^4 \ln e/e_{\text{eff}})$. For an increase in e_{eff} , the growth of the attraction of the electron to the donor can become so strong that the Mott transition from the high-conductive state to the insulating state can take place. Obviously, for this to occur the effective radius of the Bohr orbit $a_B = \hbar^2/m_e e_{\text{eff}}^2$ should be of the order of the mean distance between the impurity atoms $n^{-1/3}$. For semiquantitative estimates of the metal–insulator transition temperature, one may use the Mott criterion in its standard form $a_B n^{1/3} = 0.25$, and use equations (1) and (2).

4. Competition of Ferromagnetic and Antiferromagnetic Exchange Interactions in Manganites

Manganites possess some specific properties which are related to the fact that undoped crystals are antiferromagnetic, and they became ferromagnetic only as a result of their doping by acceptors. In other words, the superexchange is antiferromagnetic and the indirect exchange via holes ferromagnetic in them. With $x > 0.2$ they behave like degenerate ferromagnetic semiconductors at $T = 0$, i.e. the indirect exchange dominates. But the situation changes in the vicinity of the Curie point when the resistivity peak appears: as the charge carriers become localised in the band-tail states, they cannot establish the long-range ferromagnetic ordering over the entire crystal. This explains the fact that in the manganites the Curie point is located close to the resistivity peak. In initially ferromagnetic semiconductors the resistivity peak can be considerably below the Curie point, as after the charge carrier localisation, the long-range ferromagnetic ordering is supported by the superexchange. For example, in doped EuO the resistivity peak appears at about 50 K, whereas T_C of undoped EuO is about 67 K (Nagaev 1983).

At relatively small $x < 0.2$, even at $T = 0$, the manganites are in a state with a spontaneous magnetisation which is below the saturation magnetisation, and at $x = 0$ they are antiferromagnetic. As is well known, charge carriers in magnetic semiconductors tend to establish ferromagnetic ordering at which their energy is minimal. If the ordering in the undoped semiconductor is antiferromagnetic then, with increasing charge carrier density, first a magnetic state intermediate between the ferromagnetic and antiferromagnetic states should appear. At still higher densities, the ordering in the crystal becomes completely ferromagnetic. There are different points of view about the nature of the intermediate state at moderate doping (underdoped samples).

De Gennes (1960) assumed canted antiferromagnetic ordering to be an intermediate state of degenerate antiferromagnetic semiconductors. He found, treating the d-spins as classical vectors, that the canting angle should be proportional to the charge carrier density. As an alternative to canting, the electronic phase separation model was proposed (Nagaev 1972; Kashin and Nagaev 1974), according to which a degenerate antiferromagnetic semiconductor with frozen impurities in its ground state is separated into an insulating antiferromagnetic phase and a high-conductivity ferromagnetic phase. Later the case of ferro-antiferromagnetic phase separation was considered in systems with mobile impurities and a high magnetic ordering temperature (e.g. oxygen in perovskites, see Nagaev 1994). Then not only the charge carriers but also the ionised donors or acceptors are concentrated in the ferromagnetic portion of the crystal (impurity phase separation).

A mixed electronic-impurity ferro-antiferromagnetic phase separation can also be realised (Nagaev 1997a). In particular, manganites usually contain not only immobile acceptors (Ca, Sr, and so on), but also mobile acceptors in the form of excess oxygen. The situation intermediate between electronic and impurity phase separation was considered: in the ferromagnetic portion of the crystal, holes of both immobile and mobile acceptors congregate with the mobile acceptors themselves. In the antiferromagnetic portion there are no holes or mobile acceptors.

For experimental verification of these theories, the electronic phase separation theory was confirmed by electric, magnetic and magneto-optic data on EuSe, EuTe, and so on (see Nagaev 1983). On the other hand, de Gennes (1960) interpreted data (Wollan and Koehler 1955) from neutron studies of the doped lanthanum manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ as confirmation of canted antiferromagnetic ordering in them. This idea was accepted by many investigators, even those who are engaged in neutron studies, and now it is customary to refer to the Wollan and Koehler results as verification of canted ordering.

In reality, this involves a misunderstanding: Wollan and Koehler arrived at just the opposite conclusion. They pointed out that, in principle, the superposition of ferro- and antiferromagnetic peaks they observed at $x = 0.18$ can be related to either the canted antiferromagnetic ordering or a mixture of the ferro- and antiferromagnetic regions. To choose between these two possibilities, they investigated the behaviour of the peaks in the magnetic field. They found that a field of about 4 kOe halves the height of the ferromagnetic peaks but does not influence the height of the antiferromagnetic peaks.

But in the case of canted ordering, the ferromagnetism vector is rigidly related to the antiferromagnetism vector, and the field should rotate these vectors

simultaneously. Hence, both the ferro- and antiferromagnetic peaks should vary in intensity simultaneously. In contrast, in the case of the phase-separated state, the ferromagnetism and antiferromagnetism vectors are independent. This led Wollan and Koehler to conclude (which they expressed in plain words) that the phase separation, rather than canting, takes place in their samples. However, the nature of the phase separation remains as yet unknown.

Strictly speaking, a very small canting of the relativistic origin was discovered later (Matsumoto 1970) in undoped LaMnO_3 , but it has nothing in common with the charge-carrier-induced canting proposed by de Gennes (1960). Its existence was confirmed (Kawano *et al.* 1996; Hennion *et al.* 1997) by neutron investigations of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ and $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ respectively. For example, in the former at $x = 0.04$, the ferro- and antiferromagnetic peaks appear simultaneously at the same temperature (136 K), which unequivocally confirms the canted structure. But at $x = 0.125$ the ferromagnetic peaks appear at 230 K and the antiferromagnetic peaks only at 150 K (Kawano *et al.* 1996). The most natural explanation of this difference is that the ferromagnetism is not related to the antiferromagnetism as the corresponding regions are spatially separated. In other words, this result can be considered to be consistent with the conclusions of Wollan and Koehler (1955). But the hypothesis (Kawano *et al.* 1996) was advanced that, as the temperature decreases, first the ferromagnetic ordering is established and then it is replaced by canted antiferromagnetic ordering. Investigations in a magnetic field similar to those carried out by Wollan and Koehler (1955) might address the question of whether the hypothesis of van Santen and Jonker (1950) is adequate.

Hennion *et al.* (1997) discovered short-range ferromagnetic correlations with a length of several lattice constants, which were attributed to moving magnetic polarons (ferrons). This result is very important as it directly confirms phase separation: the appearance of ferromagnetic regions inside antiferromagnetic crystals. In our opinion (Nagaev 1967, 1968), these correlations should not be attributed to the moving magnetic polarons (ferrons) predicted as their number is exponentially small and they are unlikely to be observed in neutron studies. But ferromagnetic correlations can be attributed to ferrons bound to ionised acceptors. Their number is several orders of magnitude larger than the number of free ferrons.

Not only neutron data, but also electric data on manganites, conflict with the de Gennes scenario of the appearance of canted antiferromagnetic ordering due to mobile holes. In fact, contrary to the de Gennes assumption, incompletely magnetised materials are not highly conductive but insulating. In addition to Hennion *et al.* (1997), we should also mention other investigations with larger acceptor contents (see Nagaev 1996*a*). But this is not inconsistent with the properties of the phase-separated semiconductors: at modest charge carrier density they behave like insulators (Nagaev 1972, 1983; Kashin and Nagaev 1974).

From a theoretical point of view, if the isotropic exchange interaction cannot be described by an effective Heisenberg Hamiltonian, and it includes terms of higher order in spin, then the canted antiferromagnetic ordering is possible even in the absence of the Dzyaloshinskii anisotropy (Nagaev 1982). If one tries to construct such an effective Hamiltonian at $W \ll AS$, one finds that it should have such a non-Heisenberg structure. If one limits oneself to the uniform states of the crystal, then in a certain range of the hole densities the canted antiferromagnetic

ordering is more energetically favoured than the collinear antiferromagnetic and ferromagnetic orderings.

But the uniform canted antiferromagnetic ordering turns out to be unstable with respect to fluctuating static fields of ionised impurities. To make sure of this, it is sufficient to note that at the canted antiferromagnetic ordering the magneto-electric constant Γ is nonzero and rather large. In the case of double exchange and the staggered antiferromagnetic ordering at $W \ll AS$ one obtains (Nagaev 1983, 1996a)

$$\Gamma = \frac{0.3}{\nu_F^{2/3}} \left(\frac{\nu}{\nu_F} \right)^{1/3}, \quad \nu_F \sim \frac{T_C}{W} \ll 1, \quad (5)$$

where ν_F is the number of charge carriers per atom at which the ferromagnetic ordering becomes stable ($\nu < \nu_F$).

Obviously, for ν not very small (for example for ν comparable with ν_F) the quantity Γ is sufficiently close to 1 or can even exceed 1. In the former case this means that the Mott transition to the insulating state should occur contrary to the initial assumption about the metallic-like conductivity of the system. In the latter case the effective dielectric constant ζ becomes negative, and the effective charge imaginary, which also points to the instability of the uniform highly-conductive state and to the tendency of the system to a transition to the nonuniform state.

It is worth mentioning that the hypothesis (de Gennes 1960) on canted antiferromagnetic ordering contradicts not only the neutron data (Wollan and Koehler 1955), but also the electric data, according to which in the region of nonsaturated ferromagnetism manganite samples do not exhibit the metallic-like conductivity assumed by de Gennes.

However, the semiconducting conductivity is compatible with the electronic phase separation proposed by Nagaev (1972) and Kashin and Nagaev (1974) (see also Nagaev 1983). In this theory all the charge carriers are concentrated in the ferromagnetic phase, and the antiferromagnetic phase is insulating. If the volume of the former is less than the latter, the ferromagnetic phase forms high-conductive inclusions inside the antiferromagnetic host. As they are not in contact with each other, the sample as a whole is insulating. But under a magnetic field the volume of the ferromagnetic phase increases, and the inclusions begin to come in contact. Hence, the sample as a whole becomes highly conductive. This is a different mechanism of CMR from that in the completely ferromagnetic sample.

5. Role of Polarons

Here the concept of polarons in manganites used for the interpretation of manganite properties by some authors, especially by experimentalists, will be discussed. This idea does not seem very promising as the question immediately arises: if the polarons are responsible for the resistivity peak and CMR, why was this peak and CMR not observed in nonmagnetic polar crystals? As the properties of the manganites are qualitatively the same as the properties of other ferromagnetic semiconductors, one should discuss the problem in general, treating the polaron problem in detail.

The polarons cannot play a noticeable role in properties of the ferromagnetic semiconductors as the energy of lattice polarisation is considerably less than the sd exchange energy. As an example, EuS is discussed. Here the polaronic lowering of the electron energy reaches only 0.06 eV whereas the total redshift of the absorption edge due to the sd exchange amounts to 0.2 eV (Nagaev 1983). (This shift is the difference in the electron energies in the paramagnetic and ferromagnetic states.) Hence, the polaronic effects cannot play a considerable role in EuS, especially at room temperatures where their energy is comparable with the thermal energy.

A similar situation should apply in manganites. According to Loshkaryeva *et al.* (1997), the redshift for manganites in the temperature range from 345 to 95 K is 0.16 eV. Hence, the total redshift should be close to that in EuS. Unfortunately, their static and high-frequency dielectric constants appear to be unavailable in the literature. But, judging from the fact that these crystals are not very strongly polar, the polaronic energy should be comparable with that of EuS which, by the way, is the value typical of polar crystals, not only magnetic but also nonmagnetic.

More surprising is the statement by some authors that small polarons can play a decisive role in the properties of manganites. Though I was one of the pioneers of the small polaron theory (Nagaev 1961, 1962, 1963), later this concept was virtually abandoned as it was recognised that conditions for the existence of small polarons were quite unrealistic (see e.g. Nagaev 1983). According to these conditions, the bare-electron bandwidth should be small compared with the energy of lattice polarisation (a necessary condition is as follows: the energy of the lattice polarisation should exceed half the bandwidth). Even in the most polar crystals of the NaCl type, the latter is only 0.1 eV (Appel 1968), whereas the bandwidth is of order 1 eV in the double-exchange case and should amount to several eV in the opposite case where $W \gg AS$.

Strictly speaking, the value of 0.1 eV presented above corresponds to the large polaron. It is impossible to calculate the energy of a small polaron in a macroscopic approximation, as only the lattice polarisation over a length comparable with the lattice constant is essential (Nagaev 1983). Hence, the calculation requires a microscopic treatment impossible at present. Nevertheless, the result presented above can be considered as a reasonable estimate for a small polaron too. Thus, in real systems the relationship between these parameters is opposite to existence conditions for small polarons, and these conditions are violated very strongly. Initially, it was believed that small polarons exist in NiO but later it was proved experimentally that this was erroneous.

The explanation of the insulating state appearing close to T_C by formation of the small polarons does not include an answer to the question of why the polarons arise at elevated temperatures and do not exist at $T = 0$. One might try to explain this by the band narrowing occurring with decreasing magnetisation: if at $T = 0$ the condition for the existence of the small polaron was not met, it can be met at elevated temperatures. But, first, such a narrowing takes place only for the double exchange case (Nagaev 1983). In the opposite case only a shift of the band as a whole by the quantity of $AS/2$ takes place. As already pointed out (Loshkaryeva *et al.* 1997), the total redshift in manganites is about 0.2 eV. Even if one ascribes it completely to band narrowing, that would mean

that the narrowing amounts only to a few tens of a per cent. This is unlikely to be sufficient for converting a free hole into a small polaron. Similar to the JT interaction, the following argument remains in force: since the resistivity peak in the manganites is considerably lower than in other degenerate ferromagnetic semiconductors with weak polaronic effects, there is no need to invoke polarons for explaining the specific features of manganites.

There are numerous papers in which is claimed that the existence of small polarons in the manganites is proved. As an example the one by Jaime *et al.* (1997) can be mentioned. There are two reasons given for the existence of small polarons in this paper: (a) the Hall coefficient is electron-like in the paramagnetic region between $2T_C$ and $4T_C$, whereas the thermopower is hole-like, and (b) the activation energy for the Hall coefficient is less than that for the electric conductivity. However, first, the separation of the Hall coefficient in the normal and anomalous parts was not carried out by Jaime *et al.* (1997), which is vitally important in the analysis. Second, a reliable theory of the small-polaron normal Hall effect is absent at present. In numerous papers on this problem quite different results have been obtained (see Firsov 1975). In my opinion, this is a consequence of the incompleteness of the set of Wannier functions used for calculation of the Hall conductivity with the aid of the Kubo formulae (this difficulty is absent for the usual conductivity).

Moreover, the questions arise as to why, according to Jaime *et al.* (1997), small polarons appear only at temperatures exceeding twice T_C , and how a low resistivity of the order of $0.01 \Omega \text{ cm}$ typical of degenerate band-conductivity semiconductors can be reconciled with the extremely small mobility of small polarons assumed to exist here (usually one tries to apply the notion of small polarons to almost-insulating materials).

The polaronic concept was used by Zhou and Goodenough (1998) in an attempt to explain the oxygen-mass dependence of the thermopower and T_C of the manganites. The JT vibrational modes are assumed to be responsible for the polaronic effects. They are assumed to lead to the oxygen-mass dependence of the hole bandwidth below T_C which should lead to the mass dependence of the quantities investigated in Zhou and Goodenough (1998). The mechanism behind this is as follows. Above T_C , a polaron-driven phase segregation into hole-rich clusters within a hole-poor matrix is assumed to occur which can survive transition through T_C . However, the experimental data of Zhou and Goodenough alone are insufficient to confirm this scenario, and theoretical substantiation is required. The physical reason for the polaronic segregation is quite unclear. The polaronic segregation resembles, to some extent, the magnetic-electronic segregation, but in the latter case the reason for the segregation is quite obvious (see Section 4). But the basic ideas for the magnetic-electronic segregation cannot be used for justification of the electronic segregation. Second, as already pointed out, the isotope effect is likely to be caused not by the hole-phonon interaction but by the oxygen nonstoichiometry. In this case there is no reason at all to talk about the isotope dependence of the hole bandwidth.

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