Impurity-driven phase separation in degenerately doped magnetic semiconductors and high-temperature superconductors

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In this paper, the physics of phase separation in degenerately doped magnetic semiconductors and high-temperature superconductors is discussed. It is assumed that the mobility of the impurity atoms is sufficiently high to establish an equilibrium distribution of impurities throughout the crystal. This distribution can be nonuniform, which leads to nonuniform magnetic ordering and conductivity. In particular, an antiferromagnetic crystal can separate into regions with increased and decreased impurity concentrations such that the first region is ferromagnetic and the second antiferromagnetic. It is also possible for the region with increased impurity concentration to be antiferromagnetic with another type of ordering, or a spin liquid.

1. INTRODUCTION

The phenomenon of impurity-driven phase separation, which I discussed theoretically 20 years ago for degenerately doped magnetic semiconductors,[1,2] was first observed experimentally in nonsuperconducting materials. Nowadays, however, it has become one of the primary areas of research in the physics of high-temperature superconductors. The system I discussed in Refs. 1 and 2 was a frozen-in distribution of donor or acceptor impurities in a degenerately doped magnetic semiconductor (i.e., the impurity atoms were assumed to be immobile). In this case, phase separation occurs as a result of the collective self-trapping of charge carriers within regions of the normal stable phase, in which the carrier energies are lower. This effect stabilizes the unstable phase as well.

For example, in some cases ferromagnetic regions can appear in an antiferromagnetic crystal.[1–6] In other cases, an antiferromagnetic semiconductor with one structure can contain regions that are antiferromagnetic, but with a different structure (i.e., layered Landau phases within a Néel chessboard phase) or spin-liquid regions.[7]

Because all the charge carriers will concentrate in regions where the magnetic ordering is changed (e.g., to ferromagnetic order) with none of them left in those portions of the crystal with the original antiferromagnetic order, the ferromagnetic and antiferromagnetic portions of the crystal will be oppositely charged. When this is the case, a Coulomb force appears that causes intermixing of the two phases. Accordingly, these phases are no longer independent and cannot be separated, being coupled by the Coulomb force into a single system. From this standpoint, the term "phase separation," which is ordinarily used for this phenomenon, is inaccurate. Nevertheless, in what follows I will continue to use this term, describing the phenomenon by "electron phase separation."

It must be emphasized that the state described above is the ground state of the crystal, and that this distinguishes the phenomenon fundamentally from the phase separation that occurs in a first-order phase transition. In essence it is a specific state of the crystal, which is reminiscent to some degree of a Wigner crystal. On the other hand, as was shown in Refs. 3 and 4, this state can be interpreted as a superposition of nonlinear spin and charge density waves. Experimental confirmation of the existence of electron phase separation is described in Refs. 3 and 4.

A completely different type of phase separation is possible in degenerately doped semiconductors with mobile impurity atoms. Because the atoms must be mobile, this type of phase separation is usually observed only at rather high temperatures, although it can happen that considerable diffusion of impurities takes place at low temperatures due to quantum effects.[8] Furthermore, diffusion can become appreciable under the action of illumination.[8]

The mechanism of impurity-driven phase separation can operate in nonmagnetic semiconductors as well, although it will lack certain features specific to magnetic semiconductors. In nonmagnetic semiconductors, a nonuniform distribution of impurities appears spontaneously throughout the crystal, leading to nonuniformity of the crystal's electrical properties. This effect was first observed experimentally in degenerately doped Si:Li (see Ref. 8), and then in GeTe (see Ref. 9) with an excess of Te. The theoretical interpretation given by Rose *et al.*[10] was that the impurity donor atoms behave like ordinary univalent atoms and attempt to form a metal; the only difference between this "metal" and a true metal is that the electron mass and charge are renormalized by the introduction of an effective mass and a dielectric permittivity.

There is a density of impurity atoms that minimizes the energy (per impurity atom) of the impurity atom "metal." Obviously, if the true average impurity density in the crystal is lower than this density, then at $T=0$ it is energetically advantageous for the impurity atoms to concentrate within a specific region of the crystal, at which location the density is now optimal. In reality this already implies phase separation in the crystal as a whole. However, the analysis carried out in Ref. 10 showed that at

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temperatures comparable to the Fermi energy, the free energy per atom of the impurity "metal" attains the same minimum value for two different values of the impurity density. This implies that the impurity "metal" itself can in turn separate into two phases with different densities. This phase separation is a true separation, in the sense that the two phases are not coupled to one another by the Coulomb force and therefore can be separated one from the other.

For this situation, in contrast to electronic phase separation, intermixing of the phases cannot be caused by the Coulomb forces, since there are no such forces. Nevertheless, a mixed phase is possible, since the system will attempt to decrease its elastic stresses.[8,9] According to the theory of elasticity,[11] each of the phases should have a plane-parallel geometry, which is observed experimentally in EuTe.

In my view, it is not completely obvious that the elastic properties should determine the geometry of the two-phase state, since the difference between them is so slight in the two phases in the semiconductor. The state could also be nonequilibrium in nature with regard to its thermodynamics, with a geometry determined by the growth kinetics of the phases. Formation of a given single-phase region would then be a function of the distribution of seeds, and the system could be characterized by a multiplicity of regions of this phase, analogous to a polycrystalline material. In any case, the dimensions of the single-phase regions for the case of impurity-driven phase separation should greatly exceed their dimensions for electronic phase separation, both for equilibrium and nonequilibrium thermodynamic states.

Impurity phase separation in magnetic crystals will give rise to specifically magnetic behavior only if it occurs at temperatures considerably below the magnetic disordering temperature. It is clear that such a situation is most likely in magnetic semiconductors with high disordering temperatures, a class of materials to which both the high-temperature superconductors and their parent compounds belong. In these systems, two-dimensional antiferromagnetic correlations are observed even at temperatures exceeding 1000 K, while excess oxygen atoms, which play the role of acceptors, can remain mobile up to 200 K (see Ref. 12; see, also, Ref. 13).[1)]

In certain cases, phase separation in such materials clearly is accompanied by a nonuniform distribution of impurities. For example, in $La_2CuO_{4+\delta}$ below 265 K there exist two phases with $\delta=0.01$ and $\delta=0.06$, while at higher temperatures this crystal becomes uniform.[12] A new phase (ferromagnetic) phase of the high-temperature superconductor $Nd_{2-x}Ce_xCu(^{57}Co)O_4$ has been observed[14] in which the superconducting regions are nonferromagnetic while the ferromagnetic regions are nonsuperconducting.

In principle, impurity phase separation can also occur in other types of magnetic semiconductors. It is energetically advantageous for two different magnetic phases, associated with different local impurity densities, to appear if the difference between the energies of these phases is not large. This by no means always implies a low magnetic disordering temperature: it is sufficient that the system under study be not too far from the boundary between phases in the space of exchange integrals. I have discussed electronic phase separation into two antiferromagnetic phases in the vicinity of such boundaries in Ref. 7. If, however, the crystal separates into ferromagnetic and antiferromagnetic phases, the appearance of a ferromagnetic phase within a high-temperature Néel antiferromagnet is made much easier if the exchange integral between nearest-neighbor atoms is small compared to the integral between next-nearest-neighbor atoms.

On the other hand, it is possible to have equilibrium impurity-driven magnetic phase separation even in materials with low magnetic disordering temperatures if the phase that appears as a result of local increases in the impurity density has a high disordering temperature. Finally, a nonuniform impurity distribution that is created at high temperatures where the impurity mobility is high but magnetic ordering is disrupted can remain in equilibrium at low temperatures as well, where the impurities are frozen in but where magnetic ordering can exist. However, if this is not the case, i.e., the distribution of impurities is not in equilibrium at low temperatures, then electronic phase separation can occur when there is a nonuniform distribution of impurities.

The fact that phase separation is possible not only in high-temperature superconductors but also in nonsuperconducting materials implies that there is no direct correlation between phase separation and superconductivity. Nevertheless, we may conclude that phase separation makes the appearance of high-temperature superconductivity easier by creating optimal conditions for it. It is also worth pointing out that real phase separation occurs at temperatures considerably higher than the superconducting transition temperature. Therefore, the presence or absence of superconducting properties in a material should have nothing to do with the phenomenon of phase separation.

It is also worth noting that Emery *et al.*[15] have introduced a certain confusion into the problem of phase separation; these authors apparently are not familiar with the previous activity in this area. In reality, these authors have discussed electron (hole) phase separation without including the Coulomb interaction, which, as was pointed out above, plays a fundamentally important role in this phenomenon. They have attempted to justify their approach by invoking ion diffusion with charge compensation in regions where holes were concentrated. However, this mechanism of Coulomb compensation is exactly impurity-driven phase separation, and requires a completely different approach than that taken in Ref. 15: namely, a generalization of the approach used in Ref. 10. Incidentally, the ferron state, which I discovered in Ref. 16 and which Emery *et al.* rediscovered in Ref. 15, within the context of the *t–J* model, is less energetically advantageous than the magnetic string.[17]

2. AN IMPURITY "METAL" THAT PRESERVES TYPES OF MAGNETIC ORDER

In the contemporary literature, the properties of high-temperature superconductors and their parent compounds are customarily described by using the *t–J* model. However, when charge carriers and localized *d*-orbital moments are present, the more general *s–d* model can be used to this end, as discussed in Ref. 13, in which case it is equivalent to the *t–J* model. In what follows we will consider a different limiting case of the *s-d* model, corresponding to weak *s–d* coupling. Although this model is directly applicable to semiconducting compounds of rare-earth elements, it may also be suitable for high-temperature superconductors.

We can also hope that certain results obtained in this limit remain qualitatively correct in the limiting case corresponding to the *t–J* model (see Sec. 5).

In order to justify the feasibility of using the standard *s–d* model for electronic high-temperature superconductivity, we first note that the presence of a conduction electron implies replacement of one of the Cu^{2+} ions by a Cu^{+} ion in the Cu–O plane. However, the Cu^{+} ion is not necessarily found in the state $3d^{10}$, since the state $3d^{9}4s^{1}$ can turn out to be more favorable energetically when the overlap integral B_s between the *s* orbitals of adjacent atoms exceeds the integral B_d between the *d* orbitals of these atoms. Accordingly, it is possible for the minimum energy of the *s* band, given by the parameter $E_s=K_s-z|B_s|$, to lie below the bottom of the *d* band, $E_d=K_d-z|B_d|$, even though the "atomic" *s* energy K_s is larger than its *d* analog K_d (where *z* is the coordination number).

In any case, a state of delocalized conduction electrons should differ from a state of localized *d* electrons because of *s–d* hybridization. As the pressure increases, the weight of the *s* state should increase, because the orbital overlap increases with pressure faster than the change in the "atomic" energy. In those cases where the states of a conduction electron are predominantly *s*-type, the approximation of weak *s–d* coupling is certainly justified. For holes this will be true when hole motion takes place along the oxygen atom sublattice.

For definiteness we will consider an isotropic three-dimensional case. Since the impurity "metal" is analogous to an alkali metal, in which the electronic states are close to states of free electrons, the electronic states of the impurity "metal" should be close to the band states of the host crystal. Accordingly, we will use the jellium model for this "metal." Of course, such a model cannot give accurate estimates of the binding energy of the impurity "metal." However, it allows us to establish some of its behavioral regularities, e.g., the dependence of the energy and impurity density of the metal on magnetization, etc.

Let us take the Hamiltonian of the *s–d* model in the form

$$H=\sum E_{\mathbf{k}}a^{*}_{\mathbf{k}\sigma}a_{\mathbf{k}\sigma}-\frac{A}{N_t}\sum (S_{\mathbf{g}}s)_{\sigma\sigma'}\exp\{i(\mathbf{k}-\mathbf{k}')\mathbf{g}\}$$
$$\times a^{*}_{\mathbf{k}\sigma}a_{\mathbf{k}'\sigma'}-\frac{1}{2}\sum I(\mathbf{g}-\mathbf{f})S_{\mathbf{g}}S_{\mathbf{f}}+H_C, \qquad (1)$$

where $a^{*}_{\mathbf{k}\sigma}$, $a_{\mathbf{k}\sigma}$ are creation and annihilation operators for an *s*-electron with quasimomentum **k** and spin projection σ, $S_{\mathbf{g}}$ is the operator for the *d* spin of an atom with label **g**, $s_{\sigma\sigma'}$, are the Pauli matrices, and N_t is the total number of atoms in the crystal. In what follows, we will refer to the term that is bilinear in spin operators as the direct exchange Hamiltonian between magnetic atoms, although in reality it actually corresponds to superexchange between magnetic atoms. The term H_C describes the electrostatic interaction in a system of electrons and ionized donors.

In what follows, we will adopt the approach most often used in the *s–d* model, i.e., we will assume that the *s–d* exchange energy AS (where S is the magnitude of the *d* spin) is small compared to the width of the conduction band W (the *t–J* model, which corresponds to the opposite limiting case[3] $W\ll|A|S$, $A<0$, $S=1/2$, will be discussed here only qualitatively). The following conditions are assumed to be fulfilled, which are typical for degenerately doped semiconductors and which follow from the relatively small concentration n of charge carriers in them:

$$AS>\mu\gg e^2n^{1/3}/\varepsilon, \qquad (2)$$

where μ is the Fermi energy and ε is the dielectric permittivity of the crystal. All the results obtained below are independent of the sign of A. Therefore, in what follows A will be considered positive; for $A<0$ the value of A should be replaced by $|A|$.

To arrive at the essence of this problem, we shall assume a prespecified total number of donor atoms N within a total crystal volume V_t. The problem then consists of finding the optimum volume V for that portion of the crystal in which the impurities should be concentrated so as to provide a minimum of the system energy (formally, the investigation corresponds to $T=0$ because of the condition $T\ll\mu$).

In this section we will consider the case where the conduction electrons do not change the type of magnetic order in the crystal. We should keep in mind that the renormalization of the total energy of the *s*-electrons caused by *s–d* exchange is proportional to their total number N, and, therefore, may be considered as an inessential constant. Then for an antiferromagnetic crystal, the energy of the impurity metal well below the Néel point in the jellium model is given by the expression[18]

$$E_A=kN^{5/3}/V^{2/3}-aN^{4/3}/V^{1/3}-bN^{4/3}$$
$$\times(cV^{1/3}+N^{1/3})^{-1}, \qquad (3)$$

where we have adopted the notation

$$k=\frac{3(3\pi^2)^{2/3}}{10m},\quad a=3\left(\frac{3}{\pi}\right)^{1/3}\frac{e^2}{4\varepsilon},\quad b=0.05647\frac{e^2}{\varepsilon a_B},$$

$$c=\frac{0.1216}{a_B},\quad a_B=\frac{\varepsilon}{me^2}$$

(m is the effective mass of a conduction electron).

The first term in (3) corresponds to the kinetic energy of the conduction electrons, the second term to the exchange energy between electrons with parallel spins, and the third term to the correlation energy between electrons with antiparallel spins.

Differentiating E_A with respect to V leads to the following result for the optimum impurity density ν_A and energy $\lambda_A=E_A/N$ of the impurity metal per impurity atom:

$$\nu_A^{1/3}=0.145a_B^{-1};\quad \lambda_A=-0.0774me^4/4\pi\hbar^3c\varepsilon^2. \tag{4}$$

The same result remains in force for the crystal even at temperatures considerably above the Néel point. Consequently, if the mobility of the impurities is large in the paramagnetic region, then very slightly below the Néel point any low-temperature equilibrium distribution of impurities is admissible due to diffusion of the impurities at high temperatures. If the average concentration of impurities n is smaller than ν_A, then the impurity "metal" should occupy a volume $(n/\nu_A)V_t$. This part of the crystal should be highly conducting, but the rest of the crystal should be insulating.

Although both portions of the crystal have the same antiferromagnetic ordering at $T=0$, as the temperature increases the ordering in the impurity "metal" region should be destroyed more rapidly than in the insulating portion of the crystal, since at high concentrations the conduction electrons attempt to destroy the antiferromagnetic order.[3] For this reason, at increased temperatures the phase separation with respect to impurity density and electrical conductivity should be accompanied by phase separation with respect to magnetic properties. In particular, the insulating phase of the crystal should be antiferromagnetic, while the highly conducting portion should be paramagnetic.

However, the model implies completely different results for ferromagnetic crystals, since the conduction electrons are fully spin-polarized according to (2). The spin polarization causes the electron kinetic energy to be higher, and the exchange interaction stronger, than in an antiferromagnetic crystal, while the correlation energy is zero. The total energy of the impurity metal in a ferromagnetic crystal E_F is given by the expression

$$E_F=2^{2/3}kN^{5/3}/V^{2/3}-2^{1/3}aN^{4/3}/V^{1/3}. \tag{5}$$

As follows from (5), the optimum density ν_F and the energy per atom λ_F measured from $(-AS/2)$ are given by the expression

$$\nu_F^{1/3}=0.102a_B^{-1};\quad \lambda_F=-0.0475me^4/4\pi\hbar^3c\varepsilon^2. \tag{6}$$

According to (6) and (4), the optimum density in the ferromagnetic state is considerably lower than in the paramagnetic state. However, this state can be reached only by impurity diffusion below the Curie point. It is a rather peculiar fact that if we begin at low temperatures and then heat the crystal, the volume of impurity metal should increase by a factor of 3 (i.e., there is a giant negative thermal expansion).

For a ferromagnetic crystal, the conduction electrons attempt to maintain the ferromagnetic order; therefore, for $n<\nu_F$ the electrons concentrated in the region of impurity "metal" attempt to maintain ferromagnetic order in this region. Hence, at intermediate temperatures the portion of the crystal enriched by impurities can be ferromagnetic, while the rest is paramagnetic. It is worth noting that the binding energy of an impurity "metal" in a ferromagnetic crystal is considerably smaller than it is in an antiferromagnetic crystal. This implies that the probability of observing impurity phase separation in a ferromagnetic crystal is much lower than in an antiferromagnetic crystal.

3. INSTABILITY OF THE IMPURITY "METAL" FOR NONCOLLINEAR ANTIFERROMAGNETIC ORDER

Let us now consider a case where formation of the impurity "metal" within an antiferromagnetic crystal leads to the appearance of ferromagnetic order in the corresponding crystal regions. Conduction electrons, which mediate indirect exchange between local magnetic spins, attempt to establish ferromagnetic order. However, this exchange is necessarily non-Heisenberg in character, since the inequality $\mu\gg AS$, which ensures the Heisenberg type of exchange, is here replaced by the opposite limit. As a result, there exists a range of electron densities within which both the antiferromagnetic and ferromagnetic orderings are unstable. For $AS\ll\mu$ this interval contracts into a point.[3]

Let us first consider first noncollinear antiferromagnetic order as a possible candidate for stable ordering in this interval. In this interval of densities the energy of this type of ordering is doubtless below the energy of both collinear states.[3] By changing the angle 2ϑ between the moments of the magnetic sublattices, we can pass continuously from antiferromagnetic to ferromagnetic order.

Making use of (1) and neglecting the correlation energy of the electrons, we find the energy of the noncollinear two-sublattice system to second order in (AS/W) in the form

$$\begin{aligned}E_{NC}=V\Big[&2^{2/3}k(n_+^{5/3}+n_-^{5/3})-\frac{AS}{2}(n_+-n_-)\cos\vartheta\\&-2^{1/3}a(n_+^{4/3}+n_-^{4/3})-\frac{G_Q}{2}\sin^2\vartheta-\frac{S^2J}{2v}\\&\times(\cos 2\vartheta+1)\Big],\end{aligned} \tag{7}$$

where we have $J=zI$, and $I<0$ is the direct exchange integral between nearest neighbors. The following notation is used for the indirect exchange integral:

$$G_{\mathbf{Q}}=-\frac{A^2S^2}{2}\sum\frac{f_{\mathbf{k}}-f_{\mathbf{k+Q}}}{E_{\mathbf{K}}-E_{\mathbf{K+Q}}}\simeq g_{\mathbf{Q}}N,\quad g_{\mathbf{Q}}\simeq\frac{A^2S^2}{4(E_{\mathbf{Q}}-E_0)}\,. \tag{8}$$

Here f_k is the Fermi distribution function for s electrons to zeroth order with respect to AS/W, $\mathbf{Q}$ is the magnetic structure vector, and the single-electron energy E_0 corresponds to the bottom of the conduction band. The notation v is used for the volume of a unit cell, which is assumed to be simple cubic.

The densities n_+ and n_- of conduction electrons with spins up and down should be determined from the condition that their chemical potentials be equal:

$$-\frac{AM}{2}+\frac{(6\pi^2n_+)^{2/3}}{2m}=\frac{AM}{2}+\frac{(6\pi^2n_-)^{2/3}}{2m}\,,$$

$$n_++n_-=n,\quad M=S\cos\vartheta. \tag{8}$$

Now let us prove that the optimum impurity concentration cannot be achieved for noncollinear antiferromagnetic ordering. In order to verify this, we can use the Landau expansion, which corresponds to a density-induced phase transition from a nonmagnetic to a magnetized state. It follows from (7), (8′), and (3) that the energy for noncollinear ordering can be written in the following way:

$$E_{NC}=E_{At}+V\left[-\frac{3A^2n}{16\mu}-\frac{J}{v}+\frac{gn}{2}-\left(\frac{an^{4/3}}{8}\right)\left(\frac{A}{\mu}\right)\right]M^2$$
$$+4^{-3}V\left[\frac{\mu n}{4}-\frac{59}{81}an\right]\left(\frac{A}{\mu}\right)^4M^4, \tag{9}$$

where

$$E_{At}=E_A+\frac{JS^2V_t}{2}-\frac{SgN}{2},\quad \mu=\frac{(3\pi^2n)^{2/3}}{2m}\,.$$

Minimizing the energy (9) with respect to M at fixed n, we obtain

$$E_{NC}=E_{At}-V\mu_A(n-n_A)^2\theta(n-n_A)/4n_A, \tag{10}$$

where $\theta(x)$ is the Heaviside step function, $\mu_A=\mu(n_A)$ and the density n_A at which the magnetization appears is given by the following expression (terms $\propto g$ and a were omitted):

$$n_A\simeq(3\pi^2)^22^9|J|^3/3^3A^6v^3m^3. \tag{11}$$

Calculating the derivative of E_{NC} with respect to V, we find that an extremum is reached for E_{NC} at a density $n_E=4.7n_A$, however, this critical point is not a minimum, but rather an energy maximum.

We may cast some doubt on the conclusion that the impurity "metal" is unstable for skewed antiferromagnetic ordering, which follows from all this, since the value of n_E is so large, perhaps large enough that the expansion (9) may no longer be correct. Strictly speaking, we should discuss the case where n is large enough to ensure complete polarization of the electrons with respect to spin ($AM>\mu$).

In this case, according to (5), (7) the expression for the energy has the form

$$E_{NC}=E_F-\frac{S^2NG}{2}\left[1-\left(\frac{Anv}{4JS}\right)^2\right]-\frac{Vn^2vA^2}{16|J|}+\frac{JS^2N_t}{2}\,. \tag{12}$$

It follows from (12) that this energy is a maximum when

$$n_E=2^{2/3}6n_A/5,$$

which confirms the conclusions reached above.

Formally, situations are possible in which the optimum density ν_A given by (4) for an impurity "metal" in an antiferromagnetic crystal might exceed the limiting value of n_A (11) at which the antiferromagnetic order becomes unstable. On the other hand, the value of ν_F from (6) may turn out to be formally below the boundary for stability of the ferromagnetic state

$$n_F=4|J|/Av, \tag{13}$$

determined from (7) by setting the angle ϑ equal to zero there.

This implies that there is no energy minimum within the region of stability of the antiferromagnetic or ferromagnetic order, and that the minimum value of the impurity "metal" energy is reached at the corresponding stability boundaries for collinear ordering. Therefore, if the average density of donors n is smaller than n_A, but the latter is smaller than ν_A, an impurity "metal" forms with density n_A, while in the rest of the crystal there are no impurities at all. We should keep in mind that the energy minimum at ν_A has a clear-cut physical meaning in the paramagnetic region: it implies that as the temperature increases the impurity metal should change its density from ν_A to n_A.

4. COMBINED IMPURITY AND FERRO-ANTIFERROMAGNETIC PHASE SEPARATION

In this section, as part of our ongoing investigation of the possibility of separation of an impurity "metal" into phases with differing densities, we will discuss separation with simultaneous appearance of ferromagnetic ordering within the antiferromagnetic "metal." For this problem, we must now include in the impurity metal energy the energy cost due to direct exchange $D=|J|S^2$ when antiferromagnetic ordering is replaced by ferromagnetic. The equilibrium impurity density should be determined from the condition that the energy be a minimum

$$E_{FA}=E_F+DV/v-ASN/2. \tag{14}$$

It follows from (5), (14) that if the exchange energy between s-electrons exceeds the direct exchange energy between magnetic atoms, then to first approximation in D the optimum impurity density ν_{FA} is given by the expression

$$v_{FA}=v_F+18kD/a^2v. \tag{15}$$

As follows from (15), the optimum density ν_{FA} exceeds ν_F from (6).

This inequality is even stronger in the opposite limiting case of strong d–d exchange. To first order in a we obtain

$$v_{FA}=v^0_{FA}+v^1_{FA},$$

$$v^0_{FA}=\frac{1}{2}\left(\frac{3D}{kv}\right)^{3/5}, \quad v^1_{FA}=\frac{3a}{20k}(2v^0_{FA})^{2/3}. \tag{16}$$

In the latter case, to zeroth order in a the energy per impurity atom is given by the expression

$$\lambda_{FA}=(2D)^{2/5}\mu^{3/5}(v^{-1})-AS/2. \tag{17}$$

The possibility of combined impurity-magnetic phase separation is a consequence of the existence of two energy minima, one for antiferromagnetic and the other for ferromagnetic order. Let us first discuss the case where the deeper minimum in energy corresponds to ferromagnetic order, independent of whether it lies within the interval of stability of ferromagnetic order or at the stability boundary.

According to (13), (16), to zeroth order in a the first of these cases will occur when D is smaller than a certain critical value of order $(AS)^{5/2}/W^{3/2}$ (this same implication follows from (17) as well). It is worth noting that this criterion is extremely close to the condition for self-localization of conduction electrons in the ferromagnetic portion of the antiferromagnetic semiconductor, i.e., formation of ferrons[3,16]).

When the density n is smaller than $\nu_{FM}=\max\times\{n_F,\nu_{FA}\}$, i.e., the case at hand, all the impurity atoms are concentrated in the region with ferromagnetic order, which occupies a fraction n/ν_{FM} of the crystal. The remaining portion of the crystal, in which impurities are absent, is antiferromagnetic and insulating. In this regard, the situation is reminiscent of the conditions under which electron phase separation occurs,[1–6] although here there is no mutual charging of the phases or their resulting remixing on the nanometer scale.

Let us now assume that the energy minimum for antiferromagnetic ordering is deeper than that for ferromagnetic ordering. We will consider cases where the average density n exceeds the density $\nu_{AM}=\min\{\nu_A,n_A\}$ at which a minimum is possible. If n lies between the energy minimum and the stability boundary for the antiferromagnetic phase $(n_A>n>\nu_A)$, we will assume that $E_A(n)>E_{FA}(\nu_{FM})$. However, when n lies within the interval of instability of the collinear phase from n_A to n_F, we cannot make statements of this kind. In both cases, the sample should separate into two phases, with antiferromagnetic ordering in one of them and ferromagnetic ordering in the other. The impurity concentrations ζ_A and ζ_F in these phases do not coincide with ν_{AM} and ν_{FM}, and are determined by the conditions that the chemical potentials and pressures of both phases be equal:

$$\frac{\partial E}{\partial N_A}=\lambda(\zeta_A)-\lambda_{FA}(\zeta_F)+\zeta_A\frac{\partial\lambda_A}{\partial\zeta_A}-\zeta_F\frac{\partial\lambda_{FA}}{\partial\zeta_F}=0, \tag{18}$$

$$\frac{\partial E}{\partial V_A}=\zeta_A^2\frac{\partial\lambda_A}{\partial\zeta_A}-\zeta_F^2\frac{\partial\lambda_{FA}}{\partial\zeta_F}=0. \tag{19}$$

Using quadratic approximations for the energy per atom in the antiferromagnetic and ferromagnetic phases λ_A and λ_{FA} near ν_A and ν_{FA}, we can easily obtain explicit expressions for the required densities, and, consequently, the volumes of these phases V_A,V_F and the number of atoms in them N_A,N_F.

The principal difference between the previous case and the case discussed here is the fact that here it is not the ferromagnetic phase that is in the highly conducting state, but rather the antiferromagnetic phase. This is a direct consequence of the fact that the ferromagnetic ordering is less energetically advantageous than the antiferromagnetic ordering. Therefore, we find that not all of the impurity atoms are concentrated in the ferromagnetic region, but only a portion of them. However, since the concentration of impurities is higher in the ferromagnetic phase than it is in the antiferromagnetic phase, the conductivity of the first of these should be higher than that of the second.

5. COEXISTENCE OF THE ANTIFERROMAGNETIC PHASE WITH ANOTHER ANTIFERROMAGNETIC OR SPIN-LIQUID PHASE

The original antiferromagnetic phase may coexist not only with a ferromagnetic phase but with other phases in which the energy of the charge carriers is lower. In complete analogy with electron phase separation,[7] impurity phase separation is possible with the formation of a new antiferromagnetic or spin-liquid phase.

As an example, let us consider the chessboard antiferromagnetic phase with structure vector $\mathbf{Q}=(\pi,\pi,\pi)$ as the original phase, and a layered antiferromagnetic phase with the structure vector $\mathbf{Q}'=(\pi,0,0)$ for the phase that arises as a result of doping. The fact that the energy of conduction electrons in the layered phase is lower than in the chessboard phase is obvious from (7), (8).

Conditions for formation of a layered phase within the chessboard are exceptionally favorable when the undoped crystal is located in the vicinity of a boundary between these phases in the space of exchange integrals. This is possible when the direct exchange between second and third nearest neighbors is comparable in magnitude to exchange between nearest neighbors. In this case, $I_1<0$ should be close to $2I_2$, and $I_1>4I_3$ holds (see Ref. 7), where I_n is the integral for direct exchange between the nth nearest neighbors.

In contrast to ferromagnetic ordering, which can be obtained from chessboard ordering by a continuous rotation of the sublattice moments, layered ordering cannot be obtained from the chessboard ordering by continuous transformation. Therefore, the curve for the density dependence of the energy of the impurity "metal" is a simple superposition of the curves corresponding to both types of order. The curve for the chessboard order is given by Eq. (3), while the curve for the layered ordering is given by the equation

$$E'_A=E_A+D'V/v-[g(Q')-g(Q)]N, \tag{20}$$

with $D'=(-4I_1+8I_2)S^2$.

The procedure for analyzing Eq. (20) is completely analogous to that used to analyze (14); likewise it can be proved, again in a completely analogous way, that it is possible for highly conducting regions with the chessboard and layered orderings to coexist, the first having a lower, and the second a higher, concentration of impurities.

As was discussed in Ref. 7, the energy of s-electrons in the magnetically ordered spin-liquid phase is close to their energy in the layered antiferromagnetic phase. In particular, they will almost coincide if we take the electron energy E_k in the nearest-neighbor approximation. On the other hand, the energy D_{SL} consumed by disordering the spins may be considerably lower than the energy D' released by rearranging the chessboard phase into the layered phase. For example, for $I_3=0$ we have $D_{SL}=3/4D'$ at the phase boundary between the layered and chessboard phases. Therefore, in describing a spin-liquid we should replace D' by D_{SL} in (20) and $g(Q')$ by

$$g_{SL}=-A^2S^2(2\pi)^{-3}v\int d\mathbf{k}(E_\mathbf{k}-E_0)^{-1}. \tag{21}$$

For one-electron phase separation it is not possible to identify unambiguously whether the chessboard antiferromagnetic order actually can coexist with the spin liquid: in this case, it could happen that there is even more energetic advantage to coexistence with ferromagnetic ordering.[19] In order to address this question unambiguously, we must go outside of the approximations used in Refs. 7, 19 and in this paper. In any case, there is no doubt that for multielectron impurity phase separation the conditions for solving this problem tend to favor the spin liquid over the sort of self-localization of individual electrons mentioned above.

Actually, the binding energy of the impurity "metal" for a spin liquid is higher than that for ferromagnetic ordering, due to the lack of spin polarization of the conduction electrons (see expressions (4) and (6)). Therefore, we may hope that it is possible to have impurity phase separation accompanied by the appearance of a spin liquid within the antiferromagnetic semiconductor.

A special case of coexistence of antiferromagnetic phases together with the impurity "metal" phase can occur for the limiting case of the s–d model $W\ll|A|S$, $A<0$, $S=1/2$, which corresponds to the t–J model. In the view of many authors, this model is suitable both for hole-based and electron-based high-temperature superconductivity. If a chessboard antiferromagnetic ordering is observed in these systems, the charge carriers in them will be in the special autolocalized states first proposed in Ref. 17, which are now well known in the literature under the name of magnetic strings. However, the fact that the multistring problem has not yet been addressed makes the construction of a first-principles theory of phase separation difficult in these systems.

Nevertheless, certain qualitative conclusions can be drawn even at this point. As (20) shows, the energy of a string is lower within the layered phase than within the chessboard phase. For this reason, when a system is close to a phase boundary and stable ordering in the undoped crystal is chessboard-like, strings can cause impurity phase separation of the system into chessboard and layered phases, where the latter is stabilized by the magnetic strings it contains.

[1)] I have received a preprint showing that there is practically no oxygen diffusion in $YBa_2Cu_3O_{6+x}$ along oxygen-deficient planes below room temperature. Only oxygen hopping to the nearest location survives, which establishes short-range correlations.

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