Point defects and ferrons in semiconducting singlet magnets

E. L. Nagaev and A. I. Podel'shchikov

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Ferron states in magnets with singlet ground state of the magnetic ions in the crystal field are investigated. It is shown that when the ferromagnetic ion-ion exchange is close to its critical value (i.e., to the value starting with which moments are induced by the ion-ion exchange), self-trapped ferron states are always stable. In the case of antiferromagnetic ion-ion exchange between nearest neighbors, the competition of this exchange with the *s-f* exchange cause the magnetic subsystem to break up in the general case into two regions: a ferromagnetic region with variable ion moments and a noncollinear two-sublattice region with constant length of the sublattice moments and with variable angle between their directions. The effect of donor (or acceptor) defects on the properties of the singlet ferromagnet is investigated. These impurities differ from the previously studied substitutional magnetic impurity in that they have one additional characteristic length, viz., the radius of the electron orbit. It is shown that the radius of the region in which an excess magnetization is induced by a donor defect diverges at the critical value of the ion-ion exchange.

1. INTRODUCTION

One of us has shown earlier[1] that electrons from the conduction band or from inpurity local levels can produce ferromagnetic microregions in antiferromagnetic semiconductors. Free carriers can produce them at any point of the crystal, becoming self-trapped in these microregions. The electrons trapped on the impurity levels produce, naturally, ferromagnetic regions around the impurity atoms. It was also indicated in Ref. 1 that a similar situation is possible in other types of magnetic semiconductors, in which the magnetization limit is not reached, particularly in singlet magnets.

By singlet magnets are meant magnetic materials in which the total moment J of the ions differs from zero, but since the crystal lifts the degeneracy in the moment direction, all three projections of the moment vanish in the ground state, i.e., the ion behaves as if it were nonmagnetic. If the exchange interaction of the ion with the neighbors is strong enough, it causes magnetic polarization of the ions: mixing of excited states with the ground state of the ion can result in an average moment projection that is not zero, albeit not reaching saturation.

The excess mobile electron (free or trapped by the impurity center) also tends to increase the degree of magnetic polarization of the ions and to establish a ferromagnetic ordering of their moments, such that the exchange energy of the electron with the magnetic ions has a maximum gain. This is possible for a free electron if it is self-trapped in a region with increased magnetic polarization, and for an impurity electron if it produces such a region where it becomes localized by the potential of the defect. By analogy with antiferromagnetic semiconductors, one can speak in the first case of a free ferron and in the second of a localized one. The main difference between a ferron in an antiferromagnet and a ferron in a singlet magnet is that in the former case the electron changes the directions of the "ready-made" moments, whereas in the latter it changes their magnitude by magnetic polarization of the ions.

The problem of ferrons in singlet magnets became particularly pressing after experiment revealed that the phosphorus vacancies in the singlet magnet PrP induce magnetic moments,[2,3] a fact naurally explainable in terms of ferrons. Our present task is an investigation of free and localized ferrons in nondegenerate magnetic semiconductors with ions in the singlet state, viz., find the conditions for their existence and estimate their parameters.

2. FREE FERRON IN A SINGLET FERROMAGNET

We consider a mode whose Hamiltonian is

$$H=H_B+H_M+H_A, \tag{1}$$

$$H_B=B\sum_{g,\Delta,\sigma} a_{g\sigma}^{+}a_{g+\Delta\sigma}+\sum_{g,\sigma} V(g)\,a_{g\sigma}^{+}a_{g\sigma},$$

$$H_M=D\sum_{g}(J_g^z)^2-\frac{K}{2}\sum_{g,\Delta}(J_gJ_{g+\Delta}),$$

$$H_A=-A\sum_{g,\sigma,\sigma'}(J_gs)_{\sigma\sigma'}a_{g\sigma}^{+}a_{g\sigma'},$$

where $a_{g\sigma}$ are the operators of annihilation of a conduction electron with spin projection σ at the site g; Δ is the vector joining a lattice site with its nearest neighbors; J_g is the ion moment operator; $s_{\sigma\sigma'}$ are Pauli matrices, $B<0$ is the Bloch integral, $D>0$ is the crystal-field parameter, $A>0$ is the *s-f* exchange integral, and K is the direct exchange integral. In the Hamiltonian (1) H_B is the Hamiltonian of the conduction electrons with account of the field $V(g)$ of the defect, if the latter is present in the crystal. H_M stands for the Hamiltonian of the magnetic subsystem, its first term describing the influence of the crystal field and the second the exchange between the magnetic ions. The Hamiltonian H_a describes the *s-f* exchange between the conduction electron and the magnetic ions.

The Hamiltonian H_M was chosen in a form corresponding to easy-plane anisotropy. At integer moment J, however,

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it describes also singlet magnets. In fact, at $K=0$ the ground state of the ion in the crystal field is the one with $J^z=0$. Obviously, the mean values of J^x and J^y are also zero in this state. It is important that this state is nondegenerate: it is separated from the higher states by an energy gap of size D. Thus, mixing of a state having $J^z=0$ with lower states, which might yield a nonzero average moment projection, is impossible. Such a mixing can be made possible, however, by exchange of the magnetic ions with its neighbors, in which cause magnetic ordering appears in the crystal.

Since the determination of the ground state of the Hamiltonian (1) is esentially a nonlinar problem, it will be solved by a variational method. The trial function is sought in the form

$$\Phi=\left(\prod_g \psi_g\right)\left(\sum_{g,\sigma}\varphi_\sigma(g)\,a_{g\sigma}^{+}\right)|0\rangle, \tag{2}$$

where $|0\rangle$ is the vacuum state for the electrons, and $\varphi_\sigma(g)$ and ψ_g are the variational functions, normalized in unity, of the electron and of the ion g, respectively.

Factorization of the functions of the electron and of the magnetic subsystem in (2) is equivalent to the adiabatic approximation, while factorization of the functions of the individual ions is equivalent to the self-consistent-field approximation for taking the direct exchange into account.

We consider first the case of ferromagnetic ion-ion exchange $K>0$. Obviously, then, all the average moments $\langle\psi_g|J_g|\psi_g\rangle$ and the electron spin should be parallel to lie in the easy plane XY. Choosing their direction to be the X axis and putting here and elsewhere for simplicity $J=1$, we write the trial function in the form

$$\varphi_{1/2}(g)=\varphi_{-1/2}(g)=\varphi(g)/\sqrt{2},$$

$$\psi_g=\frac{1}{2}\{1-[1-M^2(g)]^{1/2}\}^{1/2}(|1\rangle_g+|-1\rangle_g)+\frac{1}{\sqrt{2}}\{1+[1-M^2(g)]^{1/2}\}^{1/2}|0\rangle_g, \tag{3}$$

where $|m\rangle_g$ is the wave function of the state in which the moment of the ion g has a projection m on the Z axis. In the state (2) and (3) the projection of the electron spin on the X axis is 1/2, and $M(g)$, which assumes the role of the variational parameter, is the mean value of the projection of the angular momentum of g in the same axis.

The mean value of the Hamiltonian (2) in the state (2), (3) is given by

$$E=B\sum\varphi^*(g)\varphi(g+\Delta)+\sum V(g)|\varphi(g)|^2+\frac{D}{2}\sum\{1-[1-M^2(g)]^{1/2}\}-\frac{K}{2}\sum M(g)M(g+\Delta)-\frac{A}{2}\sum M(g)|\varphi(g)|^2. \tag{4}$$

Minimization of (4) with respect to $M(g)$ leads to an equation for the stationary value of this parameter:

$$\frac{D}{2}\frac{M(g)}{[1-M^2(g)]^{1/2}}=\frac{A}{2}|\varphi(g)|^2+K\sum_\Delta M(g+\Delta). \tag{5}$$

At $A=0$ and $M(g)\equiv M_0$, (5) is obviously the equation for the magnetization M_0 of the crystal in the absence of a conduction electron. It is easily seen that such an equation has a nonzero solution only starting with values of K larger than a critical value K_c:

$$M_0=[1-(K_c/K)^2]^{1/2},\quad K_c=D/2z, \tag{6}$$

where z is the coordination number.

If the crystal contains a delocalized electron situated on the bottom of the conduction band, the system energy, accurate to asymptotically small terms, $\sim 1/N$ where N is the number of sites, is equal to

$$E_g=Bz-\theta(K-K_c)\left[\frac{A}{2}M_0+\frac{ND(K-K_c)^2}{4KK_c}\right], \tag{7}$$

$$\theta(t)=1 \text{ at } t>0;\ \theta(t)=0 \text{ at } t<0.$$

The energy of an electron that is self-trapped or located on an impurity level is calculated by minimizing (4) with respect to the function $\varphi(g)$. We choose as the trial function

$$\varphi(g)=\pi^{-1/2}(\beta a)^{3/2}\exp(-\beta|g|), \tag{8}$$

where the variational parameter β has the meaning of the reciprocal localization radius of the electron. We assume, in addition, the medium is continuous, meaning that $\beta a\ll 1$ (a is the lattice constant). This presupposes a small change of the magnetization $M(g)$ over the length a. The system energy reckoned from the energy (7) can then be written, in the principal order in βa, in the form

$$E=\frac{A}{4}\left[4\gamma\left(\frac{\pi}{\delta}\right)^{2/3}-\int_0^1 F_1(\delta,\varkappa;y)\,dy\right]+\bar{V}, \tag{9}$$

$$F_1=\frac{\ln^2 y}{y}\left\{\frac{\varkappa\delta}{2}M^2+yM-\delta[1-(1-M^2)^{1/2}]-\theta(\varkappa-1)\left[\frac{\delta(\varkappa-1)^2}{2\varkappa}+y\left(1-\frac{1}{\varkappa^2}\right)^{1/2}\right]\right\},$$

$$M(y)/[1-M^2(y)]^{1/2}=y/\delta+\varkappa M(y), \tag{10}$$

where $\bar{V}$ is the average potential energy in the state (8), and the following notation is used:

$$\delta=\pi D/A(\beta a)^3,\quad \gamma=|B|D^{3/2}/A^{5/2},\quad \varkappa=K/K_c. \tag{11}$$

A transformation to a new variable $y=\exp(-2\beta|g|)$ was made in (9) after replacing the summation over g by integration.

In the case of a free ferron ($V=0$) it is convenient to transform from the variational parameter β to the parameter δ (11) which is proportional to the volume of the electron-localization region. Minimizing (9) with allowance for (10), we obtain the following equation for the stationary value $\delta=\delta_m$:

$$\delta\frac{\partial E}{\partial\delta}\Big|_{\delta=\delta_m}=-\frac{A}{4}\left[\frac{8}{3}\gamma\left(\frac{\pi}{\delta}\right)^{2/3}-\int_0^1 F_2(\delta_m,\varkappa;y)\,dy\right]=0, \tag{12}$$

$$F_2=\frac{\ln^2 y}{y}\left[\delta(1-(1-M^2)^{1/2})-\frac{\varkappa\delta}{2}M^2+\theta(\varkappa-1)\frac{\delta(\varkappa-1)^2}{2\varkappa}\right].$$

The ferron state is energywise favored at $E(\delta_m)<0$. Inas-

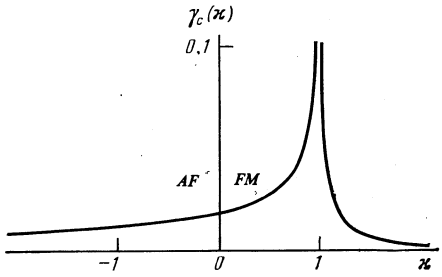

FIG. 1. Plot of the function $\gamma c(\varkappa)$.

much as only the first term of (9) depends on γ, this inequality holds if $\gamma<\gamma_c$, where γ_c is the value of γ at which $E(\delta_m)=0$. Equating the energy (9) to zero under the condition (12), we obtain the criterion for the stability of the ferron state:

$$\gamma<\gamma_c(\varkappa)=\frac{1}{4}\left(\frac{\delta}{\pi}\right)^{1/2}\int_0^1 F_1(\delta_0,\varkappa;y)\,dy, \tag{13}$$

where $\delta_0=\delta_0(\varkappa)$ is the root of the equation

$$\frac{2}{3}\int_0^1 F_1(\delta_0,\varkappa;y)\,dy=\int_0^1 F_2(\delta_0,\varkappa;y)\,dy.$$

The function $\gamma_c(\varkappa)$, obtained numerically, is shown in Fig. 1 (positive $\varkappa$ correspond to ferromagnetic ion-ion exhange). Its asymptotic values near $\varkappa=1$, where it becomes infinite, and as $\varkappa\to\infty$, are given by

$$\gamma_c(\varkappa)\approx\begin{cases}|1-\varkappa|^{-1/2}[0.021-\theta(\varkappa-1)\cdot 0.011], & |1-\varkappa|\ll 1,\\ 0.15\varkappa^{-3}, & \varkappa\gg 1.\end{cases}$$

As a result of this behavior of $\gamma_c(\varkappa)$ there always exists, at all values of the remaining parameters of the system, a region of values of $\varkappa$, in the vicinity of $\varkappa=1$, in which the ferron state is stable. The reason is that at $\varkappa\approx 1$, according to (5), a noticeable polarization of the singlet ions takes place at a small degree of localization of the electron, so that a noticeable gain in the *s-f* exchange energy is obtained with a small loss of the electron kinetic energy. Figure 2 shows plots, vs $\varkappa$, of the quantity δ_m which is proportional to the ferron volume, and of its nondimensional energy $\varepsilon=4E/A$, for different values of the system parameters.

Let us discuss the physical meaning of the foregoing results. We assume that only the ion-ion exchange integral K is variable, and the remaining parameters are fixed. The ion-ion ferromagnetic exchange enhances the ion magnetic polarization due to the self-trapped electron, so that the energy is lowered. At $\varkappa<1$, at the same time, the presence of ion-ion exchange does not lower the free-electron minimum energy (7). As a result, the enhancement of the ion-ion exchange, i.e., the growth of $\varkappa$ in the region $\varkappa<1$, makes the production of a ferron easier (the monotonic increase of γ_c with increasing $\varkappa$ in Fig. 1) and lowers the energy of the produced ferron (see Fig. 2). At $\varkappa>1$ the enhancement of the ion-ion exchange polarizes the magnetic ion almost to saturation even without the help of the electron, so that it increases the magnetization little in the localization region and acquires a very small gain of the *s-f* exhange energy upon localization. Therefore the conditions for realization of a ferron upon enhancement of the ion-ion exchange in the region $\varkappa>1$ become more stringent (monotonic decrease of γ_c with increasing $\varkappa$ in Fig. 1), and the energy of the realized ferron is decreased, so that starting with a certain value of $\varkappa$ the ferron state becomes unstable (see Fig. 2).

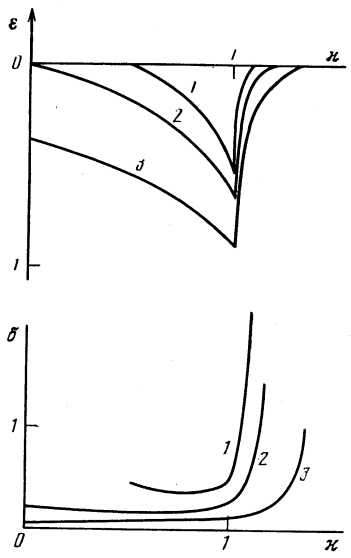

FIG. 2. The parameters of the ε and δ ferron states at the following values of γ: 1) – 0.24, 2) – 0.16, 3) – 0.08.

3. FREE FERRON IN A SINGLET ANTIFERROMAGNET

In the case of antiferromagnetic ion-ion exchange ($K<0$) the spin of the electron and the moments of the ions lie as before in the easy plane. We shall assume the electron-spin direction fixed along the X axis. The assumption that the electron spin is immobile is justified under the condition $AJ\ll W$, which is assumed satisfied (W is the width of the conduction band). This inequality makes it more difficult for the electron spin to become aligned with the angular momentum of the ion on which the electron is located than with the average magnetization (see, e.g., Ref. 1).

We shall assume for simplicity that the crystal is simple cubic. Accordingly, the magnetic subsystem will be of the Néel two-sublattice checkerboard type. In continuous-medium approximation we take the variational parameters to be the angles $2\alpha(g)$ between the directions of the angular momenta of ions belonging to different sublattices at the point g, and the values $M(g)$ of these moments. The angles $2\alpha(g)$ are generally speaking different from π, and the total moment of the sublattices is obviously also directed along the X axis. We can then write

$$\varphi_{1/2}(g)=\varphi_{-1/2}(g)=\varphi(g)/\sqrt{2},$$

$$\psi_g=\frac{1}{2}\{1-[1-M^2(g)]^{1/2}\}^{1/2}$$

$$\times[\exp(i\nu_g\alpha(g))\,|1\rangle_g+\exp(-i\nu_g\alpha(g))\,|-1\rangle_g]$$

$$+\frac{1}{\sqrt{2}}\{1+[1-M^2(g)]^{1/2}\}^{1/2}|0\rangle_g,\quad \nu_g=\exp(i\pi g), \tag{14}$$

where π is a vector with components $(\pi/a,\pi/a,\pi/a)$, so that

ν_g is equal to $+1$ or -1, depending on the sublattice to which the ion g belongs. The partition function of the ions (14) can be obtained in the following manner. For each lattice site we introduce a local coordinate system $X_g Y_g Z_g$ such that Z_g axis coincides with the Z axis of the common coordinate frame, while X_g is directed along the moment of the ion g. The local systems are then obtained from the common one by rotation through an angle $\pm\alpha(g)$ about the Z axis (the sign of the angle depends on the sublattice to which the g ion belongs). The state of the ion g in the local coordinate frame will obviously be described by the function (3). The transition from the local system to the common one leads, using the known rules for the transformation of wave functions upon rotation of the coordinate frame, to the result (14).

The wave function of the ground state of the system (2), (14) contains complex coefficients. It is easily seen, however, that complex conjugation does not change the form of the function (2), (14), since this operation is equivalent to permutation of the sublattice. Such a permutation transforms the system into itself, i.e., the ground state of the system is nondegenerate, as it should be.

The mean value of the Hamiltonian (1) in the state (2), (14) is written in the form

$$E=B\sum\varphi^*(g)\varphi(g+\Delta)+\sum V(g)|\varphi(g)|^2-{}^1/_2A\times\sum M(g)|\varphi(g)|^2\cos\alpha(g)$$
$$-{}^1/_2Kz\sum M^2(g)\cos 2\alpha(g)+{}^1/_2D\sum\{1-[1-M^2(g)]^{1/2}\}. \tag{15}$$

The energy of the crystal in the absence of an electron is described by the last two terms in (15). It is easily seen that in this case the moment M_0 of the sublattices in the ground state differs from zero if the absolute value of K exceeds the critical value K_c. Then $2\alpha(g)\equiv\pi$ (i.e., a checkerboard antiferromagnetic ordering is realized), and relations (6) are valid for M_0 and K_c.

Minimization of (15) with respect to $M(g)$ and $\alpha(g)$ leads to the following stationary values of these parameters:

$$\alpha(g)=0 \text{ and } \frac{D}{2}\frac{M(g)}{[1-M^2(g)]^{1/2}}=\frac{A}{2}|\varphi(g)|^2+KzM(g) \tag{16}$$
$$\text{at } 2|K|z<[D^2+{}^1/_4A^2|\varphi(g)|^4]^{1/2},$$
$$\cos\alpha(g)=\frac{A|\varphi(g)|^2}{2[4K^2z^2-D^2]^{1/2}} \text{ and}$$
$$M(g)=M_0=\left[1-\frac{D^2}{4K^2z^2}\right]^{1/2}$$
$$\text{at } 2|K|z>\left[D^2+\frac{1}{4}A^2|\varphi(g)|^4\right]^{1/2}. \tag{17}$$

It follows from (16) and (17) that in the case of weak exchange $|K|<K_c$ there is realized in the entire crystal a collinear ferromagnetic order of the moments that are produced as a result of the polarization of the magnetic ions by the electron. The moment of the ion g is larger the higher the effective field $h_g=A|\varphi(g)|^2/2$ acting on it. As the exchange $|K|$ increases in intensity to K_c, the situation becomes more complicated. Wherever the probability of the sojourn of the electron is large enough, the angular momenta are parallel to one another and can greatly exceed the moment M_0 in the absence of an electron. On the other hand wherever the probability of finding the electron is low, a region with a noncollinear antiferromagnetic structure is produced. The situation in this region is the same as in a Heisenberg magnet: the sublattice moments have a constant value M_0, and the angle between them at the point g is smaller the larger h_g.

From (15)–(17) we can obtain the value of the lowest energy of the system when the electron is delocalized:

$$E_g=Bz-\theta(|K|-K_c)\left(\frac{|K|}{K_c}-1\right)^2\frac{NDK_c}{4|K|}. \tag{18}$$

Using the trial function (8) and relations (15)–(17), we can express the energy of the localized state, reckoned from the energy (18), in the form

$$E=\frac{A}{4}\left[4\gamma\left(\frac{\pi}{\delta}\right)^{2/3}-\int_0^R y\ln^2 y\frac{dy}{4\delta\varkappa}-\int_R^1 G(\delta,\varkappa;y)\,dy\right]+\bar V,$$
$$G=\left[yM-\frac{|\varkappa|\delta M^2}{2}-\delta(1-(1-M^2)^{1/2})-\theta(|\varkappa|-1)\frac{\delta(|\varkappa|-1)^2}{2|\varkappa|}\right]\frac{\ln^2 y}{y}, \tag{19}$$
$$M(y)/[1-M^2(y)]^{1/2}=y/\delta-|\varkappa|M(y).$$

All the symbols have here the same meaning as in Sec. 2, and $R=0$ at $|\varkappa|<1$ and $R=\min[1.2\delta(\varkappa^3-1)^{1/2}]$ at $|\varkappa|>1$.

In the case of a free ferron ($\bar V=0$) we can again go over to the parameter δ and, following the reasoning of Sec. 2, obtain from the conditions $E=\partial E/\partial\delta=0$ a criterion for the stability of the ferron state:

$$\gamma<\gamma_c(\varkappa). \tag{20}$$

The function $\gamma_c(\varkappa)$ obtained numerically is shown in Fig. 1 (the region of negative values of $\varkappa$). The essential difference between the stability criteria of self-trapped ferron states in singlet ferro- and antiferromagnets (13) and (20) is that in the antiferromagnetic ion-ion exchange the function $\gamma_c(\varkappa)$ has no singularities. The reason is that even though the point $\varkappa=-1$ is the threshold for the appearance of moments in a singlet antiferromagnet, these moments are antiferromagnetically ordered. To increase the s-f exchange energy, a ferromagnetic order must be established, and this entails additional loss of the ion-ion energy.

As $|\varkappa|\to\infty$ we have $\gamma_c\to 1.33\cdot10^{-2}|\varkappa|^{-2/3}$. Starting from this asymptotic value and taking (11) and (20) into account, we can write down the criterion for ferron stability in the Heisenberg limit ($D=0$):

$$|B||Kz|^{2/3}/A^{5/3}<8.4\cdot10^{-3}. \tag{21}$$

The numerical coefficient in (21) is about 7% smaller in an antiferromagnet than that obtained in Ref. 1, where a different trial function was used.

The monotonic decrease of γ_c with increasing $|\varkappa|$ at $\varkappa < 0$ indicates that the enhancement of the antiferromagnetic ion-ion exchange always leads to a narrowing of the range of system parameters at which the ferron state is realized. While the ferron is stable at $K = 0$, it becomes unstable starting with a certain exchange intensity, just as in the case of a singlet ferromagnet.

Concluding the consideration of the free ferron states, we note that an external magnetic field hinders the localization of a carrier in a singlet magnet at any sign of the ion-ion exchange (see the Appendix).

4. LOCALIZED FERRONS AND THEIR INFLUENCE ON THE CRYSTAL STATE

We discuss now the influence of the charged impurities on the crystal state. In the determination of the parameters of such localized ferrons we confine ourselves to the most interesting case of ferromagnetic ion-ion exhange. In this case $V(g)$ in (1) and v in (9) are respectively equal to $-e^2/\varepsilon_0|g|$ and $-(e^2/\varepsilon_0 a)(\pi D/A\delta)^{1/3}$ (e is the electron charge and ε_0 is the static dielectric constant of the crystal). The equation for δ_m will differ from (12) in that a term $(e^2/3\varepsilon_0 a)(\pi D/A\delta)^{1/3}$ is added to the right hand side. Figure 3 shows the dependence of the energy and of the radius of the localized ferron on the direct exchange for typical values of the parameters $AJ = 0.5$ eV, $|B| = 0.4$ eV, $\varepsilon_0 = 15$, $a = 3\cdot 10^{-8}$ cm, $D = 10^{-3}$ eV. The same figure shows the energy and radius of the electron in the absence of s-f exchange and of a free ferron at the same remaining system parameters.

The characteristics of a localized ferron are determined by the simultaneous interaction of an electron with an impurity center and with the lattice ions. Each of these interactions tends to localize the electron and to lower its energy. Therefore the energy and radius of the localized ferron are smaller than those for either an impurity state in a nonmagnetic crystal or a free ferron in the region of its existence.

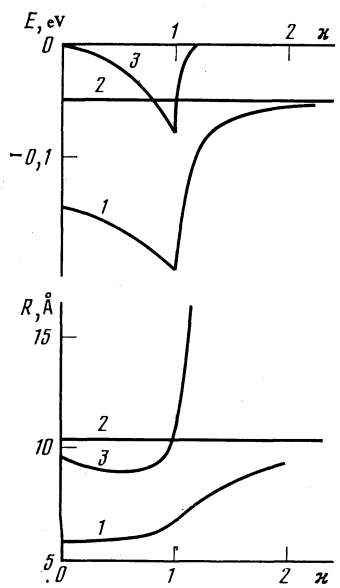

FIG. 3. Energy and radius: 1) of a localized ferron, 2) of an electron on an impurity in a nonmagnetic crystal, 3) of a free ferron.

Enhancement of the exchange at $\varkappa \gg 1$, as already indicated, leads to a decrease of the influence of the s-f exchange on the carrier state, as a result of which the parameters of the localized ferron tend as $\varkappa \to \infty$ to the parameters of the impurity state in a nonmagnetic crystal.

In nondegenerate semiconductors the density of the localized ferrons is high compared with that of the free ones. The localized ferrons can influence the magnetic properties of the crystal as a whole. We investigated earlier the effect exerted on the properties of singlet magnets of only effects such that one of the regular magnetic ions is replaced by an impurity ion with a moment that does not vanish in a crystal field.[4] We shall discuss here a similar problem for more complicated defects, viz., localized ferrons.

According to Ref. 4, exchange interaction of an impurity with nearby singlet ions induces in them an excessive magnetic moment compared with an ideal crystal. The direct exchange between the singlet ions causes this excess moment to spill over outside the effective range of the exchange of the magnetic impurity with the singlet ions. The radius of the region perturbed by the magnetic defect diverges like $|1-\varkappa|^{-1/2}$ as the critical point $\varkappa = 1$ is approached. The total excess moment of the crystal, diverges accordingly, i.e., the effective magnetic moment of the impurity becomes infinite. The reason is that near the critical point the singlet ferromagnet has a diverging magnetic susceptibility $\sim|1-\varkappa|^{-1}$. The strong influence of a magnetic impurity on the properties of singlet magnets was proved also by an experimental study.[5]

It is natural to assume that a similar situation holds also when a singlet magnet contains a localized ferron, since the distortion of the magnetic subsystem in the far zone is determined by the ratio of the crystal-field energy and the exchange energy of the singlet ions, and not by the factor that led to the onset of the initial excess moment. To verify this, we consider in greater detail Eq. (5) for the case $K > 0$. Retaining the first two terms in the expansion of the sum over the nearest neighbors,

$$\sum_{\Delta} M(g+\Delta) \approx zM(g) + a^2 \Delta M(g),$$

we rewrite it with allowance for (8) in the form

$$\frac{a^2\varkappa}{z}\Delta M + \varkappa M + \frac{1}{\delta}e^{-2\beta g} = \frac{M}{(1-M^2)^{1/2}}. \tag{22}$$

At large distances from the ferron center, the excess magnetization $m = M - M_0 (M_0 = \theta(\varkappa - 1)(1 - 1/\varkappa^2)^{1/2}$ is the magnetization of an ideal crystal) is a small parameter, and the right-hand side of (22) can be expanded in terms of this parameter. Retaining the first nonvanishing term, we obtain

$$\frac{a^2\varkappa}{z}\Delta m + \frac{1}{\delta}e^{-2\beta g} = \begin{cases} (1-\varkappa)m & \text{at } \varkappa<1, \\ \varkappa(\varkappa^2-1)m & \text{at } \varkappa>1, \\ m^3/2 & \text{at } \varkappa=1. \end{cases} \tag{23}$$

The solutions of the first two equations in (23) are combinations of terms proportional to $\exp(-2\beta g)$ and $\exp(-g/R)$, where R is equal to $a[\varkappa/z(1-\varkappa)]^{1/2}$ and $a[1/z(\varkappa^2-1)]^{1/2}$ for the cases $\varkappa < 1$ and $\varkappa > 1$, respectively. The radius of the region with increased magnetization is thus determined by the

larger of two quantities, the electron radius β^{-1} and the "magnetic" radius R. It is interesting to note that near the point $\varkappa = 1$ the multiplier of the diverging term $|1-\varkappa|^{-1/2}$ in R is larger by a factor $\sqrt{2}$ at $\varkappa < 1$ than at $\varkappa > 1$. In Ref. 4, where a different model and another calculation procedure were used, R diverges in like fashion on the right and left of the critical point.

If $\varkappa = 1$, it is natural to assume that m decreases with distance more slowly than $\exp(-2\beta g)$ (this assumption will be confirmed by the result that follows), and to neglect this term in the last equation of (23). The asymptotic solution of the resultant equation is, according to Ref. 6,

$$m(g) \to \frac{a}{g}\left(z \ln \frac{g}{a}\right)^{-1/2} \quad \text{at} \quad g \to \infty.$$

Thus, near the point of transition into the ordered state there are anomalies in the behavior of the singlet magnets if they contain not only magnetic impurities but also localized ferrons. A similar anomalously strong influence of defects on the properties of matter were investigated in systems close to the phase-transition temperature,[7,8] and in almost-magnetic metals,[9] where the exchange interaction of the conduction electrons is not much less than that required to produce a phase transition.

APPENDIX
Influence of external magnetic field on the ferron state in a singlet magnet

Assume the presence of an external magnetic field of strength $\mathscr{H}$ in energy units, directed along the X axis. Consider first the case of ferromagnetic ion-ion exchange. In the principal order of the continuous-medium approximation we can write for the energy of the localized state, reckoned from the energy of a system with delocalized electron situated on the bottom of the conduction band

$$E = B\sum \varphi^*(g)\varphi(g+\Delta) - Bz + \sum V(g)|\varphi(g)|^2 + {}^1/_2 D \sum [(1-M_0^2)^{1/2} - (1-M^2(g))^{1/2}] - {}^1/_2 Kz \sum (M^2(g) - M_0^2) - \sum (\mathscr{H}+h_g)(M(g)-M_0), \quad \text{(A.1)}$$

$$\frac{D}{2}\frac{M(g)}{[1-M^2(g)]^{1/2}} = \mathscr{H} + h_g + KzM(g), \quad \text{(A.2)}$$

$$\frac{D}{2}\frac{M_0}{(1-M_0^2)^{1/2}} = \mathscr{H} + KzM_0. \quad \text{(A.3)}$$

Equations (A.1)–(A.3) were derived in analogy with Eqs. (4) and (5), with allowance for the fact that the "electron" field $h_g = A|\varphi(g)|^2/2$ acting on the ion g is now supplemented by the external field $\mathscr{H}$. We calculate the value of $\partial E/\partial \mathscr{H}$:

$$\frac{\partial E}{\partial \mathscr{H}} = \frac{D}{2}\sum\left(\frac{M(g)M'(g)}{[1-M^2(g)]^{1/2}} - \frac{M_0 M_0'}{[1-M_0^2]^{1/2}}\right) - \frac{Kz}{2}\sum [2M(g)M'(g) - 2M_0 M_0'] - \sum (\mathscr{H}+h_g)[M'(g)-M_0'] - \sum [M(g)-M_0]; \quad \text{(A.4)}$$

where the prime denotes differentiation with respect to $\mathscr{H}$. Substituting (A.2) and (A.3) in (A.4) we obtain

$$\partial E/\partial \mathscr{H} = \sum [h_g M_0' - M(g) + M_0] = {}^1/_2 A M_0' - \sum [M(g) - M_0]. \quad \text{(A.5)}$$

From (A.3) we have

$${}^1/_2 D(1-M_0^2)^{-3/2} M_0' - KzM_0' = 1. \quad \text{(A.6)}$$

We estimate the last term in (A.5) with account taken of (A.2) and (A.3)

$$\sum (M(g)-M_0) = \sum \left[\frac{h_g + \mathscr{H} + KzM(g)}{[{}^1/_4 D^2 + (h_g + \mathscr{H} + KzM(g))^2]^{1/2}} - \frac{\mathscr{H} + KzM_0}{[{}^1/_4 D^2 + (\mathscr{H} + KzM_0)^2]^{1/2}}\right]$$

$$< \sum [h_g + Kz(M(g)-M_0)]\, {}^1/_4 D^2 [{}^1/_4 D^2 + (\mathscr{H} + KzM_0)^2]^{-3/2} = \sum \frac{2}{D}(1-M_0^2)^{3/2}[h_g + Kz(M(g)-M_0)]$$

or

$$[{}^1/_2 D(1-M_0^2)^{-3/2} - Kz]\sum (M(g)-M_0) < \sum h_g = A/2. \quad \text{(A.7)}$$

In the derivation of (A.7) we used the inequality

$$\frac{a+b}{[c^2+(a+b)^2]^{1/2}} < \frac{a}{(c^2+a^2)^{1/2}} + \frac{c^2 b}{(c^2+a^2)^{3/2}}; \quad a, a+b > 0. \quad \text{(A.8)}$$

Equations (A.5)–(A.7) yield readily the inequality $\partial E/\partial \mathscr{H} > 0$.

We consider now the case of anitferromagnetic ion-ion exchange. Generalizing Eqs. (15)–(17) we see readily that at $2|K|z < (D^2 + \mathscr{H}^2)^{1/2}$ ferromagnetic order is realized in the system and all the equations are of the same form as in the case of ferromagnetic exchange. We apply therefore the derivation given above for the inequality $\partial E/\partial \mathscr{H} > 0$. For the case $2|K|z > (D^2 + \mathscr{H}^2)^{1/2}$, however, the expression for the energy is written in the form

$$E = \sum E_g, \quad \text{(A.9)}$$

$$E_g = -\frac{h_g^2}{4|K|z} \quad \text{at} \quad |K| > K_g,$$

$$E_g = \frac{D^2}{8|K|z} + \frac{|K|z}{2} + \frac{|K|z}{2}M^2(g) + \frac{\mathscr{H}^2}{4|K|z} + \frac{\mathscr{H}h_g}{2|K|z} - \frac{D}{2}[1-M^2(g)]^{1/2} - (\mathscr{H}+h_g)M(g) \quad \text{at} \quad |K| < K_g,$$

where $K_g = [D^2 + (\mathscr{H} + h_g)^2]^{1/2}/2z$, and $M(g)$ satisfies (A.2). With (A.2) taken into account, we obtain an expression for $\partial E/\partial \mathscr{H}$:

$$\partial E/\partial \mathscr{H} = \sum (\partial E_g/\partial \mathscr{H}), \quad \text{(A.10)}$$

$$\partial E_g/\partial \mathcal{H}=\begin{cases} 0 & \text{at} \quad |K|>K_g \\ (\mathcal{H}+h_g-2|K|zM(y))/2|K|z & \text{at} \quad |K|<K_g. \end{cases}$$

Using the inequality (A.8), we estimate $M(g)$ under the condition $|K|<K_g$:

$$M(g)=(\mathcal{H}+h_g-|K|zM(g))[{}^1/_4D^2+(\mathcal{H}+h_g-|K|zM(g))^2]^{-1/2}$$

$$<\frac{\mathcal{H}+h_g}{2K_gz}+\frac{D^2}{8K_g^3z^3}(\mathcal{H}+h_g-2|K|zM(g))<\frac{\mathcal{H}+h_g}{2|K|z}$$

$$+\frac{D^2}{8K_g^3z^3}(\mathcal{H}+h_g-2|K|zM(g))$$

or

$$(\mathcal{H}+h_g-2|K|zM(g))\,(D^2|K|/4K_g^3z^2+1)>0.$$

It follows from this that the last expression in (A.10) is positive.

We have thus shown that the inequality $\partial E/\partial\mathcal{H}\geqslant 0$ holds at any sign of the exchange. This means that with increasing field the energy of the delocalized state decreases more rapidly than the energy of the localization state, and the localization of the carrier is by the same token made more difficult. A sufficiently strong external field transforms a singlet magnet into an almost saturated ferromagnet, in which no ferron states are realized.

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