

Ferromagnetic and antiferromagnetic semiconductors

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A review is given of the experimental and theoretical data on ferromagnetic and antiferromagnetic semiconductors. Information on the magnetic, electrical, and optical properties is analyzed systematically. The main theoretical ideas on the physics of magnetic semiconductors are given without detailed proof and are used in the interpretation of the experimental results relating to the influence of the magnetic order on the electrical and optical properties of magnetic semiconductors and to the influence of conduction electrons on the magnetic order.

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1. INTRODUCTION

Magnetic semiconductors are attracting increasing attention. They are very interesting from the point of view of the physics of the processes occurring in them and because of practical applications. Antiferromagnetic semiconductors have been known for some time, but the first ferromagnetic semiconductor was synthesized only in 1960.^[10] This event was of basic importance: it upset a widely held view that ferromagnetism could occur only in metals. This was followed by the synthesis of many other ferromagnetic semiconductors so that by 1970 their total number reached 50.

A special feature of magnetic semiconductors is that carriers (s electrons) interact strongly with the moments of partly filled d or f shells of magnetic ions. Therefore, magnetic order affects strongly the carrier motion and the carriers themselves may exert a strong influence on the magnetic order. It has been usual to assume that magnetic semiconductors are characterized by very narrow carrier energy bands. Then, because of the interaction between electrons and optical phonons, carriers should be small-radius polarons with a very low mobility. However, it is now found that, in typical cases, the band width in an antiferromagnetic or ferromagnetic semiconductor is of the same order as in a nonmagnetic semiconductor. Small-radius polarons may exist in magnetic semiconductors but they are more likely to be an exception rather than the rule.

Very many properties of magnetic semiconductors can be explained by the fact that the electron energy is minimal in the case of complete ferromagnetic order and that it increases on deviation from this order. The magnitude of this effect can be estimated from the observation that the absorption edge of ferromagnetic semiconductors shifts by 0.2–0.5 eV when the temperature rises to the Curie point T_c (see Figs. 2 and 3 in the next chapter). Therefore, conduction electrons tend to establish and maintain the ferromagnetic order. At low densities, electrons cannot influence the state of a crystal as a whole. However, electrons may be localized in some part of a crystal and they can then establish there a sufficiently high degree of ferromagnetic order to

achieve a strong reduction in their energy. The energy advantages resulting from self-localization in a ferromagnetic region are demonstrated in^[194,195] on the example of a conduction electron in an antiferromagnetic semiconductor. A ferromagnetic microregion created by an electron may include ~ 100 (in EuTe) or even ~ 1000 (in EuSe) magnetic atoms. In fact, a complex formed by an electron and a second-phase microregion created by it represents a new type of quasiparticle. We shall call it a ferron.¹⁾ Experimental evidence supports the existence of ferrons in antiferromagnetic semiconductors EuSe and EuTe.^[6]

Collective ferron states are possible in heavily doped magnetic semiconductors.^[46,196,197] For example, an antiferromagnetic crystal splits into ferromagnetically and antiferromagnetically ordered regions, the former with an excess and the latter with a deficiency of conduction electrons. At relatively low carrier densities in antiferromagnetic semiconductors, the ferromagnetic part of a crystal is in the form of separate droplets of ~ 10 – 100 Å radius, forming a periodic structure inside the antiferromagnetic matrix. When the carrier density is higher, antiferromagnetic droplets form a periodic structure in a ferromagnetic matrix. In the former case, the conductivity of a crystal is low because almost all the conduction electrons are locked in ferromagnetic droplets. Thus, at a critical carrier density at which the ferromagnetic part of a crystal transforms from multiply connected to singly connected, the conductivity of a crystal should rise strongly. In the case of ferromagnetic droplets in an antiferromagnetic matrix, the conductivity should increase greatly in an external magnetic field establishing a ferromagnetic order in a crystal and thus delocalizing electrons previously locked in ferromagnetic droplets.^[46,213]

¹⁾In earlier papers of the present author, [194,195] this quasiparticle was given an infelicitous name of a "magnetic polaron." M. A. Krivoglaz, who later considered the corresponding problem at $T \neq 0$, used the term "fluctuon" for states of this kind. [202] The term "ferron" reflects more accurately the physical nature of such quasiparticles, as formulated by the title of [195] "Ferromagnetic Microregions in Antiferromagnetic Semiconductors."

This splitting of degenerate antiferromagnetic semiconductors into ferromagnetic and antiferromagnetic regions was observed experimentally in EuTe^[106] and EuSe.^[212] Crystals of EuSe with carrier densities differing by a factor of five have resistivities differing by 10 orders of magnitude at 1.6°K but the application of a field of 10 kOe, which establishes a ferromagnetic order, reduces the resistance of high-resistivity samples by 10 orders of magnitude so that it becomes of the same order as that of low-resistivity samples. Magnetic measurements confirm that, in the former samples, the ferromagnetic region in the absence of the field is multiply connected, whereas in the latter it is singly connected.^[212]

Similar inhomogeneous states may exist also at elevated temperatures in heavily doped ferromagnetic semiconductors and the phase transition from the homogeneous to inhomogeneous state is usually of first order so that below the transition point the inhomogeneous state may exist in metastable form.^[82] This is qualitatively in agreement with the observations reported for EuS.^[190, 191] At lower impurity concentrations, a rise of temperature may cause a transition of a degenerate ferromagnetic semiconductor from a conducting to an insulating state due to the collective localization of electrons at donors and an increase in the degree of ferromagnetic order in their vicinity. Clearly, this explains the semimetal-insulator transition which occurs in EuO and is accompanied by a jump of the resistance by 13 orders of magnitude,^[106] which is 5–6 orders of magnitude greater than the jump of the resistance in all other known transitions of similar kind (V₂O₃, etc.). Moreover, this is the only case when an insulating phase is obtained at higher temperatures as a result of the metal-insulator transition.

Even when conduction electrons do not form inhomogeneous states in a degenerate magnetic semiconductor, they still influence strongly its magnetic properties. Thus, by varying the degree of doping of a semiconductor, we can control not only its electrical but also magnetic properties: for example, doping can double the Curie temperature of ferromagnetic semiconductors EuS and EuO (in the latter case, the Curie point may reach 140°K).^[9] Heavy doping may change an original antiferromagnetic order in a semiconductor to a ferromagnetic order. This is observed even in materials with a relatively high Néel point of ~100°K (for example, MnTe^[172]).

In contrast to magnetic metals, we cannot use the Heisenberg Hamiltonian to describe the influence of electrons on the magnetic order in a degenerate magnetic semiconductor because the Fermi energy of conduction electrons is too low. This means that magnetic structures forbidden in the Heisenberg model may, in principle, be realized in degenerate magnetic semiconductors.

Magnetic semiconductors also exhibit other unique properties. For example, a record value of the Faraday rotation of the plane of polarization of light ($\sim 3 \times 10^6$ deg/cm) is a property of a ferromagnetic semiconductor and the Faraday figure of merit is then five orders of magnitude higher than for ferromagnetic metals.^[101, 102]

We shall make a systematic analysis of the main experimental data on ferromagnetic and antiferromagnetic semiconductors and we shall present the main ideas and

results of the theory of such semiconductors. This theory is formulated in terms of the s-d model of S. V. Vonsovskii, in which all electrons in a crystal are separated into mobile s electrons and localized d electrons. In rare-earth compounds, the d electrons are understood to be the electrons in the partly filled f shells. We shall use a system of units in which temperature and magnetic field have the dimensions of energy ($kT \rightarrow T$, $2\mu_B H \rightarrow H$, $\hbar = 1$).

2. GENERAL INFORMATION ON MAGNETIC SEMICONDUCTORS

a) Magnetic Properties (Experimental Results)

1. **Ferromagnetic semiconductors (Table I).** The most interesting among europium compounds are the cubic EuO and EuS crystals with NaCl-type structure. The Eu²⁺ ions are in the ⁸S_{7/2} state and the orbital electron momentum is zero ($L = 0$, $S = J = 7/2$). For this reason and because of their weak anisotropy, these crystals are almost ideal Heisenberg ferromagnets. (According to^[214, 215], the anisotropy field in EuO is 190 Oe and that in EuS is less than 30 Oe.) The exchange is important only within the first two coordination spheres (number of neighbors $z_1 = 12$, $z_2 = 6$, respectively). The exchange integrals I_1 and I_2 of EuO are 0.63°K and -0.07°K and those of EuS are 0.20°K and -0.08°K, respectively.^[6, 96] The anisotropy constants of EuO are given in^[37]. Very valuable information on phase transitions in Heisenberg ferromagnets is obtained from measurements of the critical indices of these materials. According to^[34], the spontaneous moment of EuO near the Curie point T_C is proportional to $(T_C - T)^{0.33}$. The magnetic susceptibility of EuO above T_C is^[36, 36] proportional to $(T - T_C)^{-1.30}$, whereas, according to^[216], it is proportional to $T(T - T_C)^{-1.4}$.

TABLE I. Ferromagnetic semiconductors (T_C is the Curie point, Θ is the paramagnetic Curie point, M_0 is the moment of a unit cell)

Material	Crystal structure	T_C , °K	Θ , °K	M_0 , μ_B	Reference
CrBr ₂	Trigonal symmetry with vacancies	37	~ 37	3.85	10
EuO	NaCl, $a = 5.141 \text{ \AA}$	66.8	76	6.8	6, 11
EuS	NaCl, $a = 5.968 \text{ \AA}$	16.3	19	6.87	6
EuB ₂	—	8	4	—	18, 19, 23, 24
Eu ₂ P ₂	Ba ₂ P ₂ structure, $a = 9.026 \text{ \AA}$	25	33	6.8	22
Eu ₂ As ₂	Ditto, $a = 9.225 \text{ \AA}$	18	23	7.03	22
Eu ₂ SiO ₄	Monoclinic (ferroelastic)	5.4	—	—	16-18
EuSiO ₄	Monoclinic orthorhombic, $T < 165^\circ \text{ K}$	7	7	7	27
Eu ₂ SiO ₅	—	9	9	7	27, 30
GdN	NaCl	72	69	6, 6	6
CdCr ₂ S ₄	Spinel, $a = 10.244 \text{ \AA}$	84.5–97	135–158	5.15–5.55	9
CdCr ₂ Se ₄	», $a = 10.755 \text{ \AA}$	130–142	190–210	5.4–6	9
HgCr ₂ Se ₄	», $a = 10.753 \text{ \AA}$	108–120	192–200	5.4–5.64	9
CuCrTiS ₄	», —	4.4	0–25	—	9
CuCr ₂ Se ₃ Br	», $a = 10.416 \text{ \AA}$	274	345	5.25	9
CuCr ₂ Te ₃ I	», $a = 11.125 \text{ \AA}$	294	—	4.10	9
Dy(OH) ₂	Symmetry group C _{3i} , with $c = 3.56 \text{ \AA}$ and $a = 6.26 \text{ \AA}$ axes	3.5	4.4	—	25
Ho(OH) ₂	C_{2h} , $c = 3.53 \text{ \AA}$, $a = 6.24 \text{ \AA}$	2.5	4.2	—	25
(CH ₃ NH ₂) ₂ CuCl ₂	Perovskite	8.9	—	1	31-33

²⁾These values are taken from [6, 38, 96] and are defined so that they represent half the exchange integral in \mathcal{H}_M of Eq. (2.1).

Another important group of ferromagnetic semiconductors are chalcogenide chromium spinels. They have more complex structures than EuO or EuS and, therefore, they are less suitable for checking physical theories. However, they have much higher values of T_C (in the case of $\text{CuCr}_2\text{Te}_3\text{I}$, the Curie point lies in the room temperature range), which is very valuable from the point of view of practical applications.

There are also strongly anisotropic ferromagnetic semiconductors in which the ferromagnetic order is completely or partly due to the spin dipole-dipole interaction and the examples are $\text{Dy}(\text{OH})_3$ and $\text{Ho}(\text{OH})_3$. According to [33], in the direct vicinity of T_C the anisotropic compound $(\text{CH}_3\text{HN}_3)_2\text{CuCl}_2$ behaves as a three-dimensional strongly magnetic material but if the temperature is raised by 1°K its behavior changes to that of a two-dimensional system.

Table I includes also information on GdN and EuB_6 crystals. These materials can be synthesized only in nonstoichiometric form. Therefore, it is not clear whether their ferromagnetism is due to indirect exchange via free electrons or defect electrons.

2. Antiferromagnetic semiconductors (Table II). The number of these materials is much greater than that of ferromagnetic semiconductors and Table II gives only the properties of those materials which are most inter-

esting in respect of their electrical and magnetic properties. Information on other antiferromagnetic semiconductors can be found in [16].

Critical properties of antiferromagnetic semiconductors are reported in [14], where it is shown that the sublattice magnetizations in NiO are proportional to $(T_N - T)^\beta$ with $\beta = 0.33$. Crystals of EuTe and EuSe are isoelectronic with ferromagnetic semiconductors EuO and EuS. The former behaves as a Heisenberg antiferromagnet with $I_1 = 0.10^\circ\text{K}$ and $I_2 = -0.21^\circ\text{K}$, [38] whereas the behavior of the latter is much more complex and it can hardly be described in terms of the Heisenberg model (Fig. 1).

The phase transition of EuSe from the ordered to the disordered state at 4.6°K is of first order. Below the Néel point $T_N = 4.6^\circ\text{K}$, its antiferromagnetic structure is as follows: the spins belonging to the same plane (III) are parallel to one another and the sequence of the planes is of the $\uparrow\uparrow\uparrow$ type. [2] Below 2.8°K , EuSe changes suddenly to the ferrimagnetic state, [3, 4] which is regarded in [3, 4] as consisting of two phases, one of which is antiferromagnetic of the MnO type and the other is magnetic of the $\uparrow\uparrow\uparrow\uparrow$ type. Therefore, the resultant moment of the Eu^{2+} ion is not $7 \mu_B$ but $1.68 \mu_B$ (μ_B is the Bohr magneton). In the range $2.8^\circ\text{K} < T < 4.6^\circ\text{K}$, a weak magnetic field transforms the antiferromagnetic order to the ferrimagnetic arrangement. In fields of about 2000 Oe, the ferrimagnetic state changes suddenly to the ferromagnetic. [5, 6] Below 1.8°K , a second antiferromagnetic phase is observed. [7]

Neutron-diffraction data, [3, 4] which are used as the basis for regarding the ferrimagnetic state of EuSe as consisting of two phases, may also correspond to a canted antiferromagnetic order. In an isotropic crystal of EuSe, this order cannot be due to the relativistic effect (the weak Dzyaloshinskii-Moriya ferromagnetism is impossible). However, if the structure of the magnetic Hamiltonian is such that the terms of higher orders in spin (biquadratic, etc.) are comparable with the Heisenberg component, a canted antiferromagnetic order is possible even in isotropic crystals. [39, 40] This situation is possible, for example, if superexchange is comparable with direct exchange between magnetic atoms. The magnetic anisotropy of EuSe is very weak (~ 100 Oe) [9] and can hardly influence significantly the magnetic order.

Crystalline Eu_3O_4 is also metamagnetic. [12-14] It is strongly anisotropic and, in some respects, may be regarded as quasi-one-dimensional. The Eu^{2+} ions in a unit cell are located along the c axis, forming spin chains oriented in the same direction. Neighboring spin chains are antiparallel. A field of ≈ 2 kOe applied along the c axis orients all the chains parallel to one another. Similar behavior is exhibited by crystals of EuLu_2O_4 and EuGd_2O_4 . [15]

TABLE II. Antiferromagnetic semiconductors

Material	Crystal structure	Type of order	T_N	Θ_p	M_p , μ_B	Reference
EuTe EuSe	NaCl, $a = 6.598 \text{ \AA}$ NaCl, $a = 6.195 \text{ \AA}$	MnO	9.58 4.6	-6 9	6.7	1 2-7
Eu_3O_4	Orthorhombic Structure, $a = 10.10$, $b = 12.15$, $c = 3.51 \text{ \AA}$	Spins form ferromagnetic chains along c axis and moments of neighboring chains are antiparallel	5.3	7	7.8	12-14
EuLu_2O_4	Ditto $a = 9.49$, $b = 11.69$, $c = 3.65$		7.5	4	7	15
EuGd_2O_4	Ditto $a = 10.09$, $b = 12.11$, $c = 3.53$		4.5	2	13.3	15
Gd_3Se_3	Th_3P_4 with vacancies		6	-10	7.75	8, 9
MnO	NaCl	\uparrow to (111) ferromagnetic plane	122	-610	5.0	16
MnSe	NaCl	MnO	173	-360	5.0	16
NiO	NaCl	MnO	520	-2600	2.0	16
CoO	NaCl	\parallel {001}	291	-320	3.8	16
MnTe MnTe ₃	Hexagonal Face-centered cubic	\perp {0001} \uparrow to {001} ferromagnetic plane	323 80	-715 -520	5.0 5.0	16 16
LaMnO_3	Orthorhombic Symmetry	Type A order with alternating ferromagnetic planes	100	-500	3.9	16
CuFeS_2	Tetragonal	\parallel {001}	825			16
CoCl_2 NiCl_2	Тригональная	Ferromagnetic layers with antiparallel coupling	25 50	-37 -75	3.1 —	16 16
ZnCr_2S_4	Spinel	Weak ferromagnet	18	18		9
HgCr_4S_4	"	Helicoidal with turn angle $\varphi = 22^\circ$ at 4.2°K and $\varphi = 10^\circ$ at 30°K	60	+137, -142	5.35, 5.46	9, 10
ZnCr_2Se_4	"	With $\varphi = 42^\circ$ at 4.2°K	20	+115		9, 11

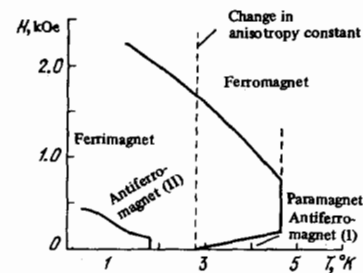


FIG. 1. Phase diagram of EuSe.

Layered magnetic materials CoCl_2 and NiCl_2 are also of interest. Introduction of graphite between the layers of magnetic atoms makes them two-dimensional Heisenberg ferromagnets.^[41] Chromium spinel HgCr_2S_4 is metamagnetic at $T < 25^\circ\text{K}$.^[9] Spinels HgCr_2S_4 and ZnCr_2S_4 are helicoidally ordered.

b) Model of a Magnetic Semiconductor

In the ground state of a magnetic semiconductor, all the outer shells of the anions are filled, outer shells of the cations are empty, and inner d and f shells of cations are only partly filled but their electrons cannot participate in charge transport processes because a strong correlation between them localized each d or f electron at its own ion. (Localization of the donor electrons is quite different: they move from atom to atom in the vicinity of a defect.) The conduction band is due to the hybridization of partly filled and completely empty states in the cation shells. Similarly, the valence band results from the hybridization of the d and f shells of the cations and the outer shells of the anions.

The Vonsovskii s-d model^[42] is very useful in a description of magnetic semiconductors. In this model, all the electrons are divided into mobile ("s electrons"), which include also the donor electrons, and localized ("d electrons" whose role in rare-earth compounds is played by the f electrons):

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_M, & \mathcal{H}_A &= -A \sum (S_g s)_{\sigma\sigma'} a_{g\sigma}^\dagger a_{g\sigma'}, \\ \mathcal{H}_B &= B \sum a_{g\sigma}^\dagger a_{g+\Delta\sigma}, & \mathcal{H}_M &= -\frac{I}{2} \sum (S_g S_{g+\Delta}). \end{aligned} \quad (2.1)$$

where $a_{g\sigma}$ and $a_{g\sigma}^\dagger$ are the operators of the creation and annihilation, at a cation g, of an s electron with a spin projection σ ; S_g and s are the spin operators of d electrons of an atom g and of an s electron, respectively; Δ is a vector joining the nearest neighbors. The spins of all the cations are equal to S.

This model can be generalized to include the orbital degeneracy of collective-state (often called itinerant) electrons, "nonfrozen" momentum of d electrons,^[44] presence of carriers of two signs, etc. However (and this point is very important), it remains valid even when the wave function of a carrier is constructed from states of the same type as localized electrons (an electron moves between d levels). In principle, in this case it is more consistent to use the Hubbard model,^[43] in which there is no separation into localized and collective-state electrons but allowance is made for the Coulomb repulsion between electrons attached to the same atom. However, we can rigorously demonstrate that, in the limit of very strong repulsion, the Hubbard model is equivalent to the special case of the s-d model ($A < 0$, $S = 1/2$).^[45]

Unless stated otherwise, the cation lattice is assumed to be simple cubic with a constant period a ($\mathbf{g} = a\mathbf{n}_x, a\mathbf{n}_y, a\mathbf{n}_z$, where $\mathbf{n}_i = 0, \pm 1, \dots$). We shall now consider the orders of magnitude of the quantities in the Hamiltonian (2.1). In the nearest-neighbor approximation (the number of such neighbors is z), the magnetic ordering energy is zIS^2 . It is of the order of $10^{-3}-10^{-1}$ eV, i.e., it is small compared with the energy of the s-d exchange AS and with the width of the conduction band $W = 2z|B|$. The latter two quantities may have a great variety of relative values. If the conduction band consists of the d states (for example, in the case of chromium spinels, this is supported by the low mobility of electrons^[107]), we usually have $AS \sim 1-10$ eV, $W \sim 0.1-1$ eV,^[54] i.e.,

$AS \gg W$. However, in some materials such as Eu chalcogenides, in which the effective mass of a carrier m^* is of the order of the free-electron mass, we have $W \sim z/m^*a^2 \sim 5-10$ eV, $AS \sim 0.5$ eV, i.e., $W \gg AS$.

Calculations aimed to determine the parameters of the Hamiltonian (2.1) are reported in several papers. An attempt is made in^[64, 65, 217] to develop a theory of superexchange in Eu chalcogenides which would explain why some of these isoelectronic compounds are ferromagnets and others antiferromagnets. A theoretical study of the magnetic anisotropy is made in^[66] and a calculation of the energy band structure of these materials is given in^[67].

In addition to the interaction with localized moments, carriers may interact strongly with optical phonons in a magnetic semiconductor. Under normal conditions, the latter is much weaker than the former. Moreover, polaron effects can occur in magnetic and nonmagnetic semiconductors and, therefore, it is not possible to explain the special properties of magnetic semiconductors by the polaron theory (with the exception of small-radius polarons discussed in Chap. 3).

c) Effective Hamiltonian of a System with Narrow Conduction Bands

Zener^[68] shows that in crystals in which magnetic atoms M are in various spin states M^{n+} and $M^{(n-1)+}$, a specific exchange interaction may occur between them due to the transfer of an electron from $M^{(n-1)+}$ to M^{n+} and back again (double exchange). Such transitions are performed by electrons in localized states, i.e., when a crystal as a whole behaves as an insulator. The energy spectrum of a system composed of two identical magnetic atoms and an electron, which can be transferred between the atoms, is found in^[69]. It is assumed there that $|B| \ll |A|S$ and $I = 0$ in the Hamiltonian of Eq. (2.1).

In the present section, we shall give the solution of the problem of the motion of conduction electrons in a crystal with a narrow ($W \ll |A|S$) band.^[70-73, 76] This problem differs from that considered in^[69] because an electron now undergoes transitions between any number (which can be large) of atoms, which interact with each other also by exchange forces of different origin ($I \neq 0$). Its solution cannot be obtained by direct generalization of the results in^[69] because, in the latter case, heavy use is made of the conservation of the total spin of a system composed of two atoms and an electron, whereas the spin for any pair of atoms in a system composed of many atoms is not conserved because of the interaction with other atoms.

The physical situation is as follows. In the zeroth approximation with respect to W/AS , we can simplify Hamiltonian \mathcal{H} of Eq. (2.1) by dropping the term \mathcal{H}_B , which describes electron transitions from atom to atom. This means that each s electron is attached to a specific atom g and because of the s-d exchange its spin is combined with the spin of this atom S_g into a spin S_{tg} , which is $S + 1/2$ for $A > 0$ and $S - 1/2$ for $A < 0$. This gives the full energy gain of the s-d exchange, which is denoted by E_A and which is $-AS/2$ for $A > 0$ and $A(S + 1)/2$ for $A < 0$ (s-d shift).

If the term \mathcal{H}_B is included, transitions of electrons from atom to atom are possible. Loss of the energy of the s-d exchange as a result of electron transitions is avoided if the electron spin rotates during the transition

so that for $A > 0$ it becomes parallel (and for $A < 0$ antiparallel) to the spin of the atom which accepts it. Thus, the motion of an electron in a crystal is equivalent to the motion of an "improper" spin $S_t = S \pm 1/2$. A quasiparticle with this spin is, in a sense, similar to a small-radius polaron and, therefore, it has been suggested^[70] that it be called a spin polaron (see Sec. b in Chap. 3).³⁾

A general approach to the problem, valid for any value of S , is developed in^[70-72]. It is easiest to describe the motion of a spin polaron when the spins of magnetic atoms can be regarded as classical vectors ($2S \gg 1$) whose direction does not change as a result of electron transitions. Each atom g is given a local coordinate system with the axis z_g directed along the spin of this atom S_g . Then, in the first approximation with respect to W/AS , the Hamiltonian (2.1) can be expressed in the nearest-neighbor approximation^[72]

$$\mathcal{H} = -AS \sum \sigma_l a_{g\sigma_l}^* a_{g\sigma_l} + B \sum \exp(2\sigma_l i \tilde{\gamma}_{gg+\Delta}) \cos\left(\frac{\theta_{gg+\Delta}}{2}\right) a_{g\sigma_l}^* a_{g+\Delta\sigma_l},$$

$$\tilde{\gamma}_{gg+\Delta} = \arctg \left\{ \cos\left(\frac{\theta_g + \theta_{g+\Delta}}{2}\right) \operatorname{tg}\left(\frac{\varphi_g - \varphi_{g+\Delta}}{2}\right) \left[\cos\left(\frac{\theta_g - \theta_{g+\Delta}}{2}\right) \right]^{-1} \right\}; \quad (2.2)$$

here, the polar angle θ_g and the "longitude" φ_g define the direction of the z_g axis in the general coordinate system; $\theta_{gg+\Delta}$ is the angle of rotation of the spin on transition between atoms, which, in this case, is equal to the angle between the spins S_g and $S_{g+\Delta}$, but the structure of the second term in Eq. (2.2) remains unchanged if these angles are not equal. If $\sigma_l = 1/2$, the electron spin is parallel and, if $\sigma_l = -1/2$, it is antiparallel to the spin of each magnetic atom encountered by an electron in its transitions.

The structure of the Hamiltonian (2.2) has a simple physical meaning. The first term represents the s-d shift which is always maximal, irrespective of the orientation of the atomic spins. It governs the effective integral of the transfer between two atoms (the coefficient in front of $a_{g\sigma_l}^* a_{g+\Delta\sigma_l}$). It is maximal for parallel spins of the atoms and vanishes for antiparallel spins. This follows because, in accordance with the structure of \mathcal{H}_B in Eq. (2.1), the transfer of an electron from atom to atom occurs subject to conservation of the spin projection σ (in the general coordinate system). Thus, if $A > 0$, the electron spin is parallel to the spin of the atom at which it is located. If the spin of the neighboring atom is directed in the same way, the electron reaching this atom still has the previous energetically favorable orientation relative to the spin of this atom. However, if the spin of the neighboring atom is opposite, the electron spin after transfer would be antiparallel to the atomic spin, which is forbidden in the approximation adopted here.

In the quantum treatment of spins, the structure of the Hamiltonian becomes much more complex. We shall reproduce the results from^[70-72] only in the two limits when the order in a crystal is close to ferromagnetic or antiferromagnetic.

A correct description of the interaction of carriers with the magnetic subsystem in such a case can be ob-

tained only if allowance is made for the participation of the carrier spins in this subsystem. As mentioned earlier, a charge carrier is equivalent to an "improper" spin $S \pm 1/2$ moving across a crystal. Therefore, the magnetic order is specific in the sense that it is realized in a system of atoms with variable magnitudes of spins.

The ideal ferromagnetic order is the one for which the total moment of the system has its maximum value. Qualitatively, this means that the spins of all the atoms are directed in the same way irrespective of whether they carry conduction electrons or not. The transfer of electrons from atom to atom simply changes the length of the spin vectors but not their direction.

The presence of a magnon in such a system means that a wave of spin deviations moves across a crystal and this happens against a background of the motion of "improper" spins $S \pm 1/2$. We shall introduce an operator b_g^* describing the creation of a magnon in an atom g and we shall define it as the operator which changes the spin projection of an atom from its maximum possible value to one which is smaller by unity; we shall also introduce an operator b_g describing the annihilation of a magnon and we shall define it as the conjugate of the creation operator; we shall assume that both operators obey the Bose relationships. This definition is invariant relative to the spin of an atom and it can be used also for variable spins. Since the Hamiltonian (2.1) conserves the projection S_T^z of the total moment of the system S_T (including the moment of the spins of conduction electrons), the same properties should be exhibited also by the total number of magnons because it is equal to $S_T - S_T^z$. Therefore, the magnon operators may occur in the Hamiltonian of the system only as even-power terms. Moreover, it is clear that since the total energy gain in the s-d exchange is obtained for any orientation of the spins S_{lg} , the magnon operators cannot occur in the term proportional to the s-d exchange integral. This is sufficient to establish the general structure of the effective Hamiltonian of the system in the spin-wave region employing the approximation which is of the first order in W/AS :

$$\mathcal{H} = \mathcal{H}_M - \frac{AS}{2} \sum \alpha_g^* \alpha_g + B \sum \alpha_g^* \alpha_{g+\Delta} + B \sum \left[\frac{b_{g+\Delta}^* b_g}{2S+1} - \left(1 - \sqrt{\frac{2S}{2S+1}}\right) (b_g^* b_g + b_{g+\Delta}^* b_{g+\Delta}) \right] \alpha_g^* \alpha_{g+\Delta} \quad (A > 0), \quad (2.3)$$

$$\mathcal{H} = \mathcal{H}_M + \frac{A(S+1)}{2} \sum \alpha_g^* \alpha_g + \frac{2SB}{2S+1} \sum \alpha_g^* \alpha_{g+\Delta} + \frac{B}{2S+1} \sum \left[b_{g+\Delta}^* b_g - 2S \left(1 - \sqrt{1 - \frac{1}{2S}}\right) (b_g^* b_g + b_{g+\Delta}^* b_{g+\Delta}) \right] \alpha_g^* \alpha_{g+\Delta} \quad (A < 0). \quad (2.4)$$

Here, α_g^* and α_g are the operators describing the creation and annihilation of spin polarons in an atom g , and these operators obey approximately the Fermi commutation relationships. The spin-dependent coefficients are found as described in^[70-72]. The change in the Hamiltonian \mathcal{H}_M due to "improper" spins is ignored in Eqs. (2.3) and (2.4) because of the inequality $zIS^2 \ll W$. The results represented by Eqs. (2.3) and (2.4) were confirmed in^[80, 81].

In the antiferromagnetic case, the creation of a magnon represents the deviation of a spin from the direction of the sublattice moment. Since the sublattice moments are antiparallel, the projection of the total moment of the system cannot be expressed in terms of the total number of magnons and, therefore, it is not an integral

³⁾One example is CdCr_2Se_4 , in which the appearance of an electron in the conduction band corresponds to the replacement of one of the regular Cr^{3+} ions with Cr^{2+} . In view of the translational invariance of the crystal, an electron migrates from one Cr ion to another in such a way that Cr^{2+} seems to move along the crystal. An erroneous view is sometimes held that transition of a Cr^{3+} ion to the Cr^{2+} state represents the capture of an electron by a local level.

of motion. The term free of the magnon operators drops out in this case because, in accordance with Eq. (2.2), electron transitions without a change in the spin direction are forbidden for $\theta_{gg+\Delta} = \pi$ and the expansion of the effective Hamiltonian in terms of magnons begins directly from linear terms^[76]

$$\mathcal{H} = \mathcal{H}_M - \frac{AS}{2} \sum \alpha_g^* \alpha_g + \frac{iB}{\sqrt{2S+1}} \sum e^{i(\pi \cdot g)} (b_{g+\Delta} + b_g^*) \alpha_g^* \alpha_{g+\Delta} \quad (A > 0), \quad (2.5)$$

$$\mathcal{H} = \mathcal{H}_M + \frac{A(S+1)}{2} \sum \alpha_g^* \alpha_g + \frac{iB\sqrt{2S}}{\sqrt{2S+1}} \sum e^{i(\pi \cdot g)} (b_{g+\Delta}^* + b_g) \alpha_g^* \alpha_{g+\Delta} \quad (A < 0), \quad (2.6)$$

where, for a simple cubic lattice, the relevant vector is $\pi \equiv (\pi/a, \pi/a, \pi/a)$. The presence of terms linear in respect of magnons in Eqs. (2.5) and (2.6) is explained qualitatively in Sec. b of Chap. 4.

De Gennes^[74] suggested earlier a Hamiltonian for a magnetic semiconductor which agrees with Eq. (2.2) if we assume $\tilde{\gamma}_{gg+\Delta} = 0$ for all such terms. It follows that the de Gennes Hamiltonian is valid only at $T = 0$. It is clear from Eqs. (2.5) and (2.6) that the error in the Hamiltonian (2.2) for $\theta_{gg+\Delta} = \pi$ is, if the spin rotation is allowed for, $1/\sqrt{2S+1}$ and not the error in the classical approximation $1/2S$. It follows that the presence of a magnon in an atom represents rotation of the atomic spin by an angle $\sim 1/2S$. The terms in the Hamiltonian proportional to the number of magnons in an atom, i.e., b^*b , are consequently of the order of $1/2S$ [see, for example, Eqs. (2.3) and (2.4)]. However, the Hamiltonians (2.5) and (2.6) are not quadratic but linear in terms of the magnon operators and, therefore, the coefficients in front of these linear terms are $\sim 1/\sqrt{2S}$ in the limit $S \rightarrow \infty$. If for real values of the spins the inequality $1/2S \ll 1$ is still satisfied, we in practice have $1/\sqrt{2S+1} \sim 1$. Therefore, the application of Eq. (2.2) to antiferromagnets may result in serious errors.

3. NONDEGENERATE FERROMAGNETIC SEMICONDUCTORS

a) Optical, Electrical, and Photoelectric Properties

Ferromagnetic semiconductors have very special electrical and optical properties due to the presence of spontaneous magnetization. These properties include particularly the giant shift of the fundamental absorption edge E_g , which occurs when the temperature is lowered and which begins before the appearance of the spontaneous polarization. All ferromagnetic semiconductors, with the exception of CdCr_2Se_4 , exhibit a shift in the red direction amounting to several tenths of an electron volt when the temperature is altered by 10–100°K, i.e., the rate of this shift is one or two orders of magnitude faster than in ordinary semiconductors (see, for example,^[6, 9, 125]).

The application of a magnetic field H reduces the shift near T_c but this has little influence on the position of the edge in the limit $T \rightarrow 0$. Figure 2 shows the dependence of the absorption edge of EuS on T and H .^[6] The shift for EuO reaches 0.25 eV, reducing the gap by 25%.^[85] The effect is strongest in HgCr_2Se_4 (Fig. 3) whose gap decreases by a factor of three.^[86]

The red shift is proportional to the change in the magnetization only at temperatures T much lower than T_c . It occurs also at $T > T_c$ and the total shift in the paramagnetic region is of the same order as in the ferro-

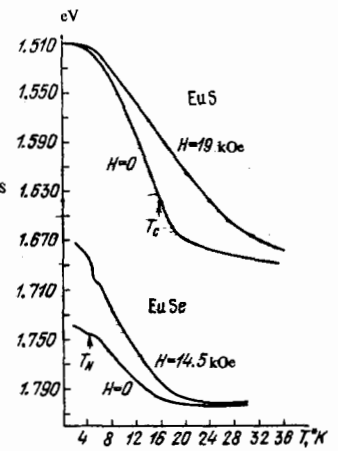


FIG. 2. Temperature dependences of the position of the absorption edge E_g of EuS and EuSe.

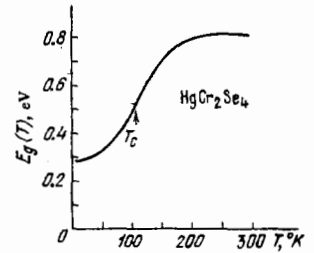


FIG. 3. Temperature dependence of the position of the absorption edge of HgCr_2Se_4 .

magnetic state. The energies of the absorption edge at $T \gg T_c$ of some ferromagnetic semiconductors are as follows: 1.1 eV for EuO, 1.65 eV for EuS,^[6] 1.57 eV for CdCr_2S_4 , 1.32 eV for CdCr_2Se_4 , and 0.84 eV for HgCr_2Se_4 .^[125]

The Faraday rotation of the plane of polarization in a ferromagnetic semiconductor reaches higher values than in ferromagnetic metals and the Faraday figure of merit (rotation per unit attenuation of the light intensity) of ferromagnetic semiconductors is five orders of magnitude greater than the corresponding figure of metals. The Faraday rotation in EuO near 0.61μ is 8.5×10^5 deg/cm.^[100] The rotation in EuS reaches a record value (Fig. 4): at 8°K in a field 11.5 kOe it is 1.1×10^6 deg/cm and 1.5×10^6 deg/cm for peaks near 2.1 eV and 4.3 eV, respectively. Extrapolation of these values to the total saturation of the magnetic moment gives 2×10^6 deg/cm and 2.7×10^6 deg/cm.^[101, 102]

Electrical properties of pure crystals have not been investigated thoroughly and the results obtained are sometimes contradictory. Thus, according to^[103, 104], the conductivity of pure EuO crystals at 300°K is $\sim 10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$ and its activation energy is 0.60 eV. However, according to^[105], the activation energy varies from 0.55 to 1.1 eV, depending on the purity of the sam-

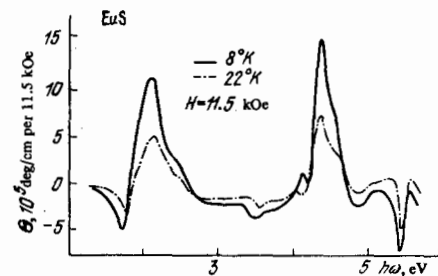


FIG. 4. Faraday rotation in EuS.

ple. Shallow donor levels are characteristic of EuO: the Gd impurity gives rise to levels of 0.017 eV depth (at $T \gg T_C$).^[112] The levels of anion vacancies in EuO are considerably lower. Shallow levels are due to the high permittivity ϵ_0 of EuO (23.9 eV).^[123] The levels in EuS are deeper because ϵ_0 is 13.2 eV.^[124]

Moderately doped paramagnetic semiconductors are characterized by a nonmonotonic dependence of the electrical resistivity ρ on the temperature T , shown in Fig. 5a for n-type $\text{Cd}_{0.99}\text{In}_{0.01}\text{Cr}_2\text{Se}_4$.^[107] Similar results are reported also for EuO and EuS with moderately high donor concentrations^[109-112] (see Fig. 18 in Chap. 6).

It is clear from Fig. 5a that the normal Hall coefficient R_0 can behave in the same way as the resistivity ρ but the thermoelectric power exhibits anomalies in the vicinity of T_C . The Hall mobility of electrons $\mu_H = R_0\rho^{-1}$ is low, between 0.1 and $10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$, which shows that the electron band is narrow.

It is established in^[113] that the behavior of holes in p-type CdCr_2Se_4 differs very greatly from the behavior of electrons in n-type CdCr_2Se_4 . The hole mobility is much higher than the electron mobility: in the region of 160°K, the hole mobility reaches $200 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$. In contrast to n-type crystals, the resistivity of p-type crystals does not pass through a maximum near T_C but falls monotonically with rising temperature (similarly, no peak is exhibited near T_C by p-type EuO crystals annealed in an oxygen atmosphere).^[109] Moreover, n-type crystals exhibit a very high negative transverse magnetoresistance (near T_C a field of 10 kG changes the resistance by an order of magnitude), whereas the transverse magnetoresistance of p-type crystals is 2-3 orders of magnitude lower and it is negative below T_C but positive above this temperature. According to^[118], the longitudinal magnetoresistance of p-type crystals behaves quite differently at $T < T_C$ than the transverse effect: in very weak electric fields, it is negative but it rises with the electric field in the range from 30 to 300 V/cm and becomes positive (Fig. 5b). It depends on the orientation of the fields relative to the crystallographic axes of a sample. Above $T_C = 130^\circ\text{K}$, the effect disappears (it vanishes actually at 135°K), i.e., it is clearly due to the long-range magnetic order. The positive magnetoresistance may possibly be accounted by an enhancement of spin waves by the holes heated in the electric field.^[118]

All these data indicate that the interaction of holes with the spins of magnetic atoms is much weaker than

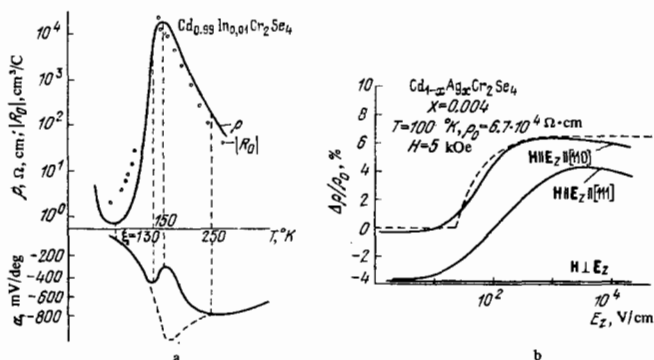


FIG. 5. Temperature dependences of the resistivity, thermoelectric power, and Hall coefficient of n-type CdCr_2Se_4 (a) and field dependence of the magneto-resistance of p-type CdCr_2Se_4 (b).

the interaction of electrons and it is clearly not the dominant mechanism of the hole scattering at $T \gtrsim T_C$. Holes in CdCr_2Se_4 move mainly between nonmagnetic atoms, whereas electrons move between magnetic atoms. As pointed out in^[113], the negative magnetoresistance of n-type CdCr_2Se_4 is not only due to an increase in the order as a result of application of this field but also due to a downward shift of the bottom of the conduction band.

It should be pointed out that it is difficult to interpret the Hall effect data for ferromagnetic semiconductors because of the need to separate the normal and anomalous Hall effects. This is done in^[113,120] on the assumption that the relevant constants are independent of the magnetic field. However, it is shown in^[113] that, in the case of n-type CdCr_2Se_4 , this procedure is invalid due to the strong nonlinear field dependence of the effect. It is assumed in^[119,121,122] that the anomalous Hall effect in EuO and EuS is negligible. This assumption seems to be justified because it is confirmed by direct experimental measurements at $T \ll T_C$, when the anomalous Hall effect should be highest.^[121]

Many ferromagnetic semiconductors are also photoconducting and this can be used in obtaining the information on the conductivity of pure crystals at low temperatures when direct measurements cannot be made. The photosensitivity curve is generally different from the absorption curve. The absorption edge of EuS corresponds to the frequency at which the photosensitivity falls to half its maximum value. The shape of the photosensitivity curve depends weakly on temperature but its maximum shifts with temperature in accordance with the same law as the absorption edge.^[6] The maximum sensitivity rises with the field H and the effect increases in strength on approach to T_C . Different types of temperature dependence of the maximum sensitivity have been reported by various authors probably because of the different amounts of imperfections in the crystals employed. For the sake of comparison, the temperature dependences of the photosensitivity of EuO and EuS taken from^[6] are plotted in Fig. 6 and the dependences taken from^[131-134] are plotted in Fig. 7.

There are no noticeable minima in the photoconductivity near T_C in Fig. 7, whereas the minimum for EuS in Fig. 6 is deep. This is due to the use of higher quality EuS crystals in^[131]. An investigation of the Hall effect of photoconducting EuO^[134] has shown that the carriers are electrons. Figure 8 shows the magnetic-field dependences of the photoelectron mobility μ_H in EuO.^[134]

The photoconductivity is also exhibited by CdCr_2Se_4 ^[135-140] and, in contrast to EuO and EuS, an additional maximum is observed in the photosensitivity

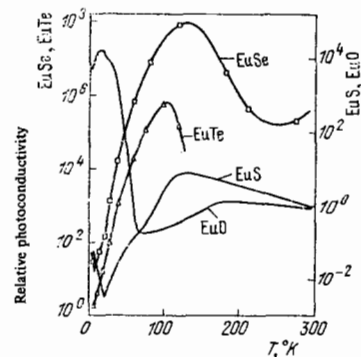


FIG. 6. Temperature dependences of the photoconductivity of EuO, EuS, EuSe, and EuTe. [6]

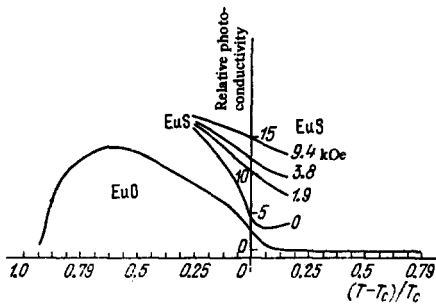


FIG. 7. Temperature dependences of the photoconductivity of EuO and EuS. [131-134]

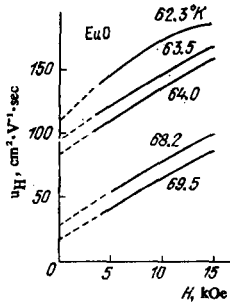


FIG. 8. Magnetic-field dependence of the electron mobility in EuO.

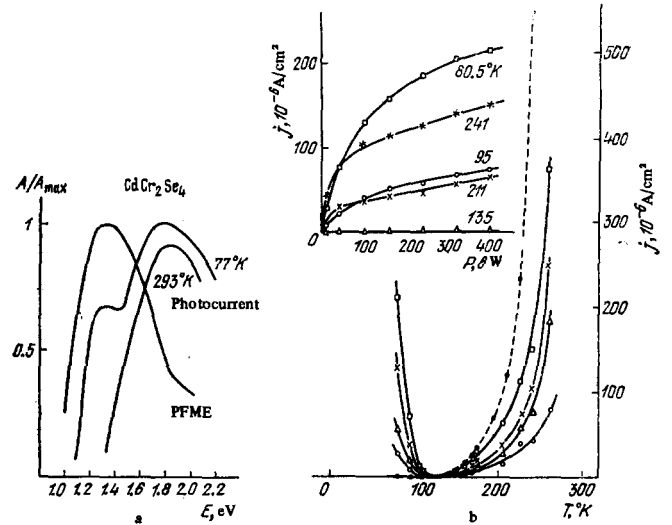


FIG. 9. Spectral dependences of the photoconductivity and photoferrimagnetic effect (PFME) in CdCr₂Se₄ (a) and photoresponse of CdCr₂Se₄ plotted as a function of the incident light power P and temperature (b).

curve below T_c (Fig. 9a).⁴⁾ According to [136], the photoconductivity of pure crystals is weak and it rises strongly on introduction of 1% Ga. Near T_c , the photoconductivity passes through a deep minimum (Fig. 9b). The photo-magnetoresistance of CdCr₂Se₄ is positive [232] with a maximum at T_c .

b) Spectrum of Carriers in Ferromagnetic Semiconductors with Narrow Bands

In this and the next section, we shall consider the energy spectrum of free carriers in a ferromagnetic semiconductor with the aim of explaining the principal relationships governing the red shift. It is convenient to begin this discussion from the case of narrow bands $W \ll AS$, which is known to apply to chromium spinels. It is clear from Eqs. (2.3) and (2.4) that, if $A < 0$, the interaction with spins of magnetic atoms appears even at $T = 0$, when there are as yet no magnons: it reduces by a factor of $1 + 1/2S$ the effective Bloch integral and, consequently, the width of the energy band of carriers, which is inversely proportional to the effective mass. This result is obtained in [70] and its confirmation can be found in [77, 78]; it resembles the increase in the mass of carriers in polar crystals due to the electron-electron interaction. Physically, it is due to the fact that the state with the maximum projection of the total spin of an atom g and an electron carried by this atom, $S_t = S - 1/2$, is the superposition of two states: $S_g^z = S$, $\sigma = -1/2$ and $S_g^z = S - 1$, $\sigma = 1/2$. However, if $\sigma = 1/2$, an electron cannot be transferred to a neighboring atom with a spin projection $S_{g+\Delta}^z = S$ because the spins of the atom $g + \Delta$ and of the electron carried by it would be parallel to one another and their total spin would be $S + 1/2$. Therefore, electron transitions occur only when the projection of the electron spin assumes the value $\sigma = -1/2$. Conse-

quently, the lifetime τ of an electron in an atom increases and the band width decreases proportionally to τ^{-1} . If $A > 0$, an electron has a fixed spin projection $\sigma = 1/2$ and transitions are always possible, i.e., there is no renormalization of the spectrum at $T = 0$.

This problem was considered earlier in [79] for $A < 0$; however, because of incorrect allowance for the s-d exchange, the results reported there are incorrect: it is predicted that the s-d shift does not reach $A(S + 1)/2$ and the width of the carrier band is exponentially small. Thus, the energy of the ground state obtained in [79] is considerably higher than that given by Eq. (2.4) and this shows that the results in [79] are inaccurate.

The influence of temperature on the carrier spectrum can readily be found from Eqs. (2.3) and (2.4) in the first order of the perturbation theory in respect of the parameter $1/2S$, which is assumed to be small. The temperature-dependent electron energy \tilde{E}_k (k is the crystal momentum) is given by the expression (s-d shift is omitted):

$$\tilde{E}_k = z\tilde{B}\gamma_k, \quad \tilde{B} = B \left[1 + \frac{1}{2SN} \sum_q (\gamma_q - 1) m_q(\omega_q^0) \right], \quad (3.1)$$

$$\omega_q^0 = J(1 - \gamma_q), \quad J = zIS, \quad \gamma_k = \frac{1}{z} \sum_{\Delta} e^{i(k \cdot \Delta)},$$

where m_q is the magnon distribution function. It is clear from the system (3.1) that, when T increases, the effective Bloch integral decreases, i.e., the bottom of the spin-polaron band shifts upward. At $T = J$, this shift is proportional to $T^{5/2}$, i.e., it is weaker than the change in the magnetization.

At higher temperatures in the range $J \ll T \ll JS$, the shift is proportional to T , i.e., to the change in the magnetization in this temperature range. At temperatures T_c and higher, only approximate characteristics of the electron spectrum such as the electron density moments can be found. [72] It follows from the analysis of these characteristics that the shape of the electron band does not change greatly even for $2S \gg 1$. The second moment near T_c is 1.22 times smaller and in the limit $T \rightarrow \infty$ it is 1.42 times smaller than at $T = 0$. If we assume that the shift of the fundamental absorption edge depends similarly on temperature, it then follows that this shift

⁴⁾The author is grateful to V. G. Veselago for supplying this figure.

should be governed by the correlation of the nearest neighbors and its total value in the range $T \gg T_c$ should be $\sim 60\%$ of the shift between 0 and T_c (the experimental value is even greater—Fig. 3).

The coherent-potential method is used in [78] to show that, if $A < 0$, the width of the carrier band in the limit $T \rightarrow \infty$ is $\sqrt{S+1}/\sqrt{2S+1}$ times smaller than $2z|B|$ so that for $S \gg 1$ the result reduces to the second moment in [72].

c) Spectrum of Carriers in Ferromagnetic Semiconductors with Wide Bands

In the $W \gg AS$ case (for example, EuO or EuS), it must be noted that the electron energy is not an analytic function of AS/W . [89,90] We can readily show that the expression $\tilde{E}_{k\sigma} = E_k - AS\sigma$ (S is the average magnetization per atom), obtained from Eq. (2.1) in the first approximation with respect to AS/W , is invalid if the direction of the local moment varies slowly in space. For example, in a helicoid with a vector q , the energy of an electron of momentum k found by a classical analysis of spins ($2S \gg 1$) is given by the exact expression: [92]

$$\tilde{E}_k = \frac{E_k + E_{k+q}}{2} \pm \frac{1}{2} \sqrt{(E_k - E_{k+q})^2 + A^2 S^2}, \quad E_k = zB\gamma_k \quad (3.2)$$

(this expression was obtained even earlier for $q = \pi$ in [218]). We shall consider this energy in the limit $W \gg AS$. Clearly, for $k \rightarrow 0$ and $q \ll q_0 = \sqrt{2m^*AS}$ ($1/m^* = 2|B|a^2$), the s-d exchange energy gain is $-|A|S/2$, i.e., it is equal to the gain obtained in a ferromagnet although we now have $\bar{S} = 0$. The physical reason for this is that, if $q \ll q_0$, the electron spin follows adiabatically the direction of the local magnetic moment and becomes aligned with this moment so that the full gain in the energy of the s-d exchange is achieved at all points in a crystal. If the projection of the electron spin were to remain constant, a helicoidal structure would have been "seen" by an electron as a periodic alternation of potential humps and wells and, in the case of sufficiently large values of AS and small values of q , an electron might be captured in one of the wells. However, if the spin is aligned with the local magnetic moment, an electron moves freely in a crystal: at each point, the s-d interaction potential corresponds to the bottom of the potential well. Thus, if $q \ll q_0$, an electron is indeed in a spin-polaron state. If $q \gg q_0$, its spin is no longer able to follow the magnetic moment and the s-d shift vanishes in the first order with respect to AS/W . Clearly, Eq. (3.2) cannot be applied to a ferromagnetic semiconductor but it helps us to understand better the results obtained below.

In the spin-wave region, we find that, as in the case of spin polarons, a correct description of the electron-magnon interaction is obtained by introducing "proper" magnons allowing for the participation of the spin of a conduction electron in fluctuations of the total moment of the system. As in Eqs. (2.3) and (2.4), the electron-magnon Hamiltonian may be quadratic in respect of the operators of the "proper" magnons because of conservation of their number. Such a Hamiltonian can be obtained for $2S \gg 1$ as follows: the Holstein-Primakoff transformation of the spin operators to the magnon form is followed by the canonical transformation in the Hamiltonian (2.1), which removes, in the first order with respect to $1/2S$, the terms which are linear for magnons. [89,92] In the most interesting case of a ferromagnetic semiconductor, when all electrons are spin-

polarized at $T = 0$, the transformed Hamiltonian corresponding to $A > 0$ becomes

$$\mathcal{H} = \sum (E_k - \frac{AS}{2}) a_{k\uparrow}^* a_{k\uparrow} + \sum \omega_q^2 b_q^* b_q + \sum C_{kqr} a_{k\uparrow}^* a_{k-r\uparrow} b_q^* b_{q+r}, \quad (3.3)$$

$$C_{kqr} = \frac{A}{4N} \left(\frac{E_{k+q} - E_k}{AS + E_{k+q} - E_k} + \frac{E_{k+q} - E_{k-r}}{AS + E_{k+q} - E_{k-r}} \right)$$

[at $T \neq 0$, the transformed operators $a_{k\uparrow}^*$ and $a_{k\uparrow}$ in Eq. (3.3) correspond to a state in which the spin is parallel to the moment of a crystal only in zeroth order with respect to $1/2S$].

In the first order with respect to $C_{kqr} \sim 1/2S$, we find that Eq. (3.3) yields an expression for $\tilde{E}_{k\uparrow}$ which is identical with Eq. (3.1) if $T \ll T_0 = J_0^2 a^2$, i.e., the energy shift is proportional to $T^{5/2}$. This means that up to T_0 , when only magnons with $q \ll q_0$ are important and the moment varies slowly in space, an electron is in a spin-polaron state. In the range $T \gg T_0$, the expression for the electron energy obtained from Eq. (3.3) in the first order with respect to C_{kqr} can be conveniently represented in the form

$$\tilde{E}_{k\uparrow} = E_k - \frac{AS}{2} - \frac{Aq_0^2}{2N} \sum_q \frac{m_q}{q^2 + q_0^2}, \quad \bar{S} = S - \frac{1}{N} \sum_q m_q. \quad (3.4)$$

The last term in Eq. (3.4) allows for the "cutoff" of the interaction between electrons and long-wavelength magnons. At temperatures $T \gtrsim T_c/S$, this term is of the order of $AS\sqrt{AS/W}/T_c$, i.e., in the main order with respect to $\sqrt{AS/W}$ it can be ignored; then, the s-d shift in this range is $-AS/2$ and this result can be obtained formally from Eq. (2.1) using the perturbation theory in the first order in H_A . It corresponds to an electron state in which the spin is directed along the average moment of the crystal. This means that, at temperatures $T \gg T_0$, spin polarons dissociate in a wide-band ferromagnetic semiconductor. However, under real conditions, the inequality $\sqrt{AS/W} \ll 1$ is poorly satisfied and the contribution of the last term in Eq. (3.4) is important.

These results are in qualitative agreement with the experiments: it is clear from Fig. 2 that, at low temperatures, the absorption edge of EuS is practically unaffected by temperature variation whereas, at higher temperatures, it varies, like the magnetization \bar{S} , linearly with T .

On approach to T_c , when the magnetization \bar{S} decreases, the relative importance of the last term in Eq. (3.4) rises, i.e., once again the long-wavelength fluctuations begin to play the dominant role. The s-d shift can be estimated by a classical analysis of the spins. [93]

An electron migrating from atom to atom generally changes the direction of its spin. The angle θ by which the spin is rotated should minimize the energy, which consists of the translational term $E_B \sim W$ and of the s-d shift E_A . According to Eq. (2.2), the maximum gain in E_B , equal to $-z|B|$, corresponds to $\theta = 0$. However, then the s-d shift vanishes. On the other hand, the maximum s-d shift is obtained if the spin of an electron at each atom is parallel to the atomic spin. However, since the angles between the spins of neighboring atoms are fairly large at $T \sim T_c$, this would have resulted in a considerable loss in E_B . Therefore, it follows from the condition $W \gg AS$ that the angle θ should be sufficiently small.

This condition can be satisfied by assuming that the spin of an electron at each atom g is directed along the moment $M_g = \sum_{\Omega_g} S_g$ of a region Ω_g of radius $R \gg a$

centered on the atom in question. Since regions Ω_g and $\Omega_{g+\Delta}$, associated with two neighboring atoms, overlap strongly, the angle between their moments is small and tends to zero in the limit $R \rightarrow \infty$.

On the other hand, since the correlation length κ^{-1} near T_c is large, the average projection $\langle S_g^z \rangle$ of the spin S_g onto the direction M_g is positive and, consequently, the s-d shift is $E_A = -(A/2)\langle S_g^z \rangle$. This shift decreases with rising R because of the increase of the contribution to M_g of those atoms which are located far from the atom g and whose spins are correlated less strongly with S_g . Therefore, R can be regarded as a variational parameter.

The average energy of the s-d exchange of an electron with an atom at which it is located is given by

$$\bar{E}_A = -A \langle \bar{s} S_g \rangle \approx -\frac{A}{2} \frac{\langle \bar{M}_g S_g \rangle}{M} \quad (M = |\bar{M}_g|), \quad (3.5)$$

since the electron spin s is directed along the moment M_g (the bar represents thermodynamic averaging). According to Eq. (2.2), the bottom of the conduction band is separated from its center by

$$\begin{aligned} \bar{E}_B &\approx -z|B| \cos \frac{\theta_{gg+\Delta}}{2} \approx -z|B| + \frac{z|B|F}{4}, \\ F &= \left(1 - \frac{\langle \bar{M}_g M_{g+\Delta} \rangle}{M^2}\right), \quad \cos \theta_{gg+\Delta} = \frac{\langle \bar{M}_g M_{g+\Delta} \rangle}{M^2}, \end{aligned} \quad (3.6)$$

where $\theta_{gg+\Delta}$ is the angle between the directions of the neighboring moments; the phases $\tilde{\gamma}_{gg+\Delta}$ are unimportant for low values of $\theta_{gg+\Delta}$.^[93]

Spin correlation functions are described by Ornstein-Zernicke expressions which, subject to a suitable selection of $\kappa(T)$, are valid up to T_c :^[99]

$$\overline{S_p S_h} = \frac{b S^2 e^{-\kappa h}}{h}, \quad b = \frac{a^3}{4\pi r_1^2}, \quad r_1 \sim a. \quad (3.7)$$

We can easily see that, in the limit $\kappa \rightarrow 0$, we have

$$\overline{S_g M_g} \sim \int_{\Omega_g} \frac{d^3 r}{r} \sim R^2, \quad M^2 \sim \int_{\Omega_g} \frac{d^3 r d^3 r'}{|r-r'|} \sim R^5,$$

so that \bar{E}_A of Eq. (3.5) is proportional to $1/\sqrt{R}$. The quantity \bar{E}_B in Eq. (3.6) is proportional to R^{-2} because F can be expanded in terms of Δ/R and the results should be even in Δ and should vanish in the limit $R \rightarrow \infty$. Minimizing the energy $\bar{E}_A \pm \bar{E}_B$ with respect to R , we obtain the following estimate for the energy gain due to the s-d exchange:

$$\Delta E_{sd} \approx -0.8 (A^2 S^2 b \sqrt{m^*})^{2/3} \sim -AS (AS/W)^{1/3}. \quad (3.8)$$

The numerical factor in Eq. (3.8) can be found by a more rigorous method.^[93] In this method, the Hamiltonian (2.1) is used and a term is separated whose eigenfunctions are plane waves with fluctuating spin which is aligned to the direction of the local moment. This moment is defined as the moment of regions Ω_g whose radii are selected so as to ensure minimum energy for the states under consideration. An estimate obtained in^[93] for the damping and corrections to the spectrum due to the rest of the Hamiltonian justifies the use of plane waves with fluctuating spin as the zeroth-approximation states.

An estimate of the energy gain of Eq. (3.8) for the s-d shift can be obtained also by summing graphs of the one-electron Green function, corresponding to $k = 0$ in all orders of the perturbation theory with respect to AS/W ,

which can be done in the Ornstein-Zernicke approximation in the limit $\kappa \rightarrow 0$ to within a constant ~ 1 .^[94]

If AS/W is small for $AS = 0.5$ eV and $W = 5$ eV (EuO, EuS), then $(AS/W)^{1/3}$ is of the order 1. Therefore, the s-d shift near T_c is, in spite of the absence of spontaneous magnetization, still fairly large although the random fluctuations reduce it by a factor $\sim (AS/W)^{1/3}$ compared with a helicoidal structure in the limit $q \rightarrow 0$ given by Eq. (3.2). In contrast to the $W \ll AS$ case, the shift is governed by the correlation of the more distant rather than the nearest neighbors. The s-d shift decreases with rising temperature and in the range $T \gg T_c$ it becomes $\sim (AS)^2/W$, in agreement with the perturbation theory developed in terms of AS/W in^[87, 95].

According to Eq. (3.8), the shifts of the absorption edge are of the same order of magnitude in the range $T < T_c$ and $T > T_c$ provided $(AS/W)^{1/3} \sim 1$, which is in agreement with the experimental results (Figs. 2 and 3). According to the theory,^[87, 95] the former shift should be W/AS times as high as the latter. It is interesting to note that, if $W \ll AS$, the shift of the energy may be of the same order as for $W \gg AS$ since it is governed by the larger of the two quantities W or AS (see Sec. b).

In the case under discussion, the shift of the absorption edge is in the direction of the red wavelengths, because at temperatures $T < T_c$ an electron is transferred optically to a lower spin-split conduction subband. However, in some cases, for example, in CdCr_2S_4 , the shift is in the blue direction. For example, if at $T = 0$ all the d spins are directed in the same way and the absorption is due to the transfer of a d electron to the s band, it enters the subband with the same spin direction. However, depending on the sign of the s-d exchange integral, this subband may be lower or higher.

d) Local Electron and Magnon Levels, and Carrier Density

In discussing localized states of carriers, we shall confine ourselves to the case in which the radius of an impurity state is equal to the lattice constant. The influence of a localized electron on the magnetic order near a donor is considered in^[115] using the following model: an electron joins a central atom to z of its neighbors forming a magnetic molecule, which can be considered separately from other atoms in a crystal and which is described by the Hamiltonian

$$\mathcal{H}_m = -s (A_0 S_0 + A_1 \sum_{\Delta} S_{\Delta}), \quad (3.9)$$

where S_0 , S_{Δ} , and s are the operators of the spin of a defect, its neighbors, and an electron; A_0 and A_1 are exchange integrals multiplied by the probability that an electron is residing at a given atom.

We can easily see that, if we ignore the direct exchange between magnetic atoms, the Hamiltonian (3.9) is obtained from the Hamiltonian of the s-d model (2.1) in the first order in \mathcal{H}_A if the zeroth-approximation is taken to be the Hamiltonian \mathcal{H}_B with an additional term describing the interaction between an electron and a defect. Thus, the condition of the validity of the model described by Eq. (3.9) is the smallness of the sum $A_0 S_0 + z A_1 S$ compared with the lowest excitation energy of a donor E_d .

It is shown in^[116, 89, 90] that in the spin-wave range the thermal shift of a local level is considerably less than that of the bottom of the conduction band since a local

ferromagnetic order in the vicinity of a donor is considerably higher than the average order in a crystal. Thus, the depth of a local level increases with rising temperature. At high temperatures, $T \gg T_c$, the depth begins to decrease again because the magnetic order in the crystal as a whole is already destroyed and the energy of a free carrier is independent of temperature. However, the magnetic order in the vicinity of a defect is not yet fully destroyed.

However, in the limit $T \rightarrow \infty$ the effective depth of a donor level $E_d(T)$ is greater than at $T = 0$.^[90] For example, in the case of a defect such that an electron is most likely to be localized on atoms in the first coordination sphere, its energy is governed by the average moment L of the z nearest neighbors of the defect. This moment is not zero although it is directed completely at random (the quantity L/zS governs the relative fluctuations of the moment, which, in accordance with the principles of statistical physics, should be $\sim 1/\sqrt{z}$). The electron spin becomes aligned parallel to this moment and, therefore, for any direction we achieve a gain in the s-d exchange energy. The application of the results of^[115] to $z = 12$ and $S = 7/2$ gives, in the limit $T \rightarrow \infty$, the value $L = 12$, i.e., the high-temperature s-d shift considered in the model of Eq. (3.9) is $-AL/2z$,^[90] which represents 30% of its value at $T = 0$. If $AS = 0.5$ eV, the depth of a level of this kind is ~ 0.1 eV greater at $T \gg T_c$ than at $T = 0$. At lower temperatures, when the depth of the level passes through a maximum, this difference is even greater: it may be close to $AS/2$. The general expression for the carrier density and, therefore, for the depth of a level at $T \gg T_c$ is obtained in^[89, 90].

Since the activation energy of extrinsic conduction passes through a maximum, this should give rise to singularities in its temperature dependence not exhibited in the intrinsic conduction case, when the activation energy varies monotonically with temperature. In fact, at low temperatures the rise of the depth of a level with temperature, $E_d(T)$, may give rise to a resistivity minimum in the low-temperature region corresponding to $(d/dT)(E_d/T) = 0$.^[117, 111, 112, 90] Above this temperature range, the carrier density decreases with temperature. The existence of this minimum automatically implies the existence of a resistivity maximum in the region of T_c because, at $T \gg T_c$, the density is known to rise with temperature (the activation energy decreases with increasing T). This can explain the anomalous temperature dependences of the resistivity exhibited by ferromagnetic semiconductors and shown in Figs. 5 and 18.

An increase in the coupling between magnetic atoms in the vicinity of a defect, due to the indirect exchange via a localized electron, may give rise to local or quasi-local magnons in the magnon spectrum. The influence of such defects on the magnon spectrum is considered in^[116, 89, 90]. The molecular field approximation and the Hamiltonian (3.9) are used in^[115] to calculate the high-temperature magnetic susceptibility of an extrinsic ferromagnetic semiconductor. The increase in this susceptibility because of the presence of magnetic quasimolecules is interpreted in terms of the paramagnetic Curie point θ , which is temperature-dependent. Thus, quasimolecules not only increase θ but also cause a deviation from the Curie-Weiss law (see also^[116]). The Curie point shifts by a much smaller amount. Such effects have been observed experimentally.^[128-130]

e) Transport Phenomena in Nondegenerate Ferromagnetic Semiconductors

It is natural to expect the transport phenomena in nondegenerate ferromagnetic semiconductors to be governed primarily by the interaction of carriers with the d spins. The standard transport theory and Eqs. (2.3), (2.4), and (3.3) yield the following expression for the relaxation time (the scattering of carriers by magnons can be regarded as elastic because of the large difference between their effective masses):^[70, 45, 142]

$$\left. \begin{aligned} \tau_k^{-1} &= \frac{ka}{2\pi N} \sum_q f_q m_q (1 + m_q), \\ f_q &= \frac{9|B|}{S^2} (1 - \gamma_q)^2 \quad \text{for } W \ll AS, \\ f_q &= \frac{A^2 q^4}{4(q_0^2 + q^2)^2 |B|} \quad \text{for } AS \ll W. \end{aligned} \right\} \quad (3.10)$$

It is clear from Eq. (3.10) that spin polarons in a narrow-band semiconductor interact very weakly with magnons ($\tau_k \propto T^{-4}$) in the range $T < T_c/S$; at temperatures $T > T_c/S$, the interaction is much stronger ($\tau_k \propto T^{-2}$). Similarly, the scattering of carriers in wide-band semiconductors changes, when the temperature is raised, from the T^{-4} to the T^{-2} law.

The results represented by Eq. (3.10) in the $W \gg AS$ case differ from those obtained in^[125, 141, 163, 164], where the same problem is tackled by the "cutoff" of the interaction between electrons and long-wavelength magnons. At temperatures $T \gg T_c$ subject to the inequality

$$AS \ll \sqrt{WT},$$

ensuring that the electronic damping is weak,^[93] we can use the results obtained in^[125, 141]:

$$\tau_k^{-1} = \frac{1}{2} \pi A^2 S^2 g(E_k),$$

where $g(E_k)$ is the density of electron levels. In the narrow-band case, the mobility u can be calculated in the range $T \gg T_c$ only if a much stronger inequality $T \gg W$ is obeyed. It follows from the Kubo formula that although in this case the concept of crystal momentum of a carrier is meaningless, the mobility is still given formally by the same expression as in the band theory ($u = e\tau/m^*$) if we substitute $\tau^{-1} = 2T$.^[45, 73, 143]

The behavior of the resistivity ρ near T_c presents the most difficult problem. At first sight, it would seem that, like the neutron scattering, the carrier scattering should be strongest near the Curie point. In fact, the cases of neutron and electron scattering are physically very different: neutrons pass through a crystal experiencing only isolated collisions, whereas collisions of electrons with spins are so frequent that the state of an electron changes radically. An example of this behavior is demonstrated in Sec. c: the electron spin becomes aligned with the direction of the local moment.

Numerous experiments carried out on pure ferromagnetic metals have shown that there is no maximum of the resistivity ρ at the Curie point T_c but the derivative $d\rho/dT$ has a singularity of the same type as the specific heat. In contrast to metals, ferromagnetic semiconductors usually exhibit a resistivity peak near T_c . However, in analyzing the resistivity results, we must bear in mind that the direct measurement is possible only in the case of fairly heavily doped samples, whose behavior may differ very considerably from the behavior of perfect crystals (see Sec. a in Chap. 4). The critical scattering in perfect crystals, whose resistivity

is very high, is best deduced from the photoconductivity. In particular, it is evident from Figs. 6 and 7 that there is no photoresistivity peak near T_c of EuO. In the case of those EuO crystals which do exhibit a peak of ρ , it is found that this peak lies at a temperature T which is slightly higher than T_c and, moreover, its relative amplitude depends very strongly on the defect concentration (see Fig. 18). This shows that the peak of ρ is due to defects. Further experimental studies of the resistivity of pure samples are needed to obtain clearer information on this point.

A calculation of the scattering of electrons by critical fluctuations near T_c carried out in the Born approximation shows that the scattering should be strongest at T_c .^[146] However, in the same approximation, the electron damping has a logarithmic divergence at T_c , which shows that this approximation is inapplicable in the range $T \sim T_c$.^[91]

It is pointed out in^[146] that the contribution of the long-wavelength correlations of the d spins to the electron scattering should have a cutoff because only the spins separated by distances not exceeding the mean free path can scatter coherently. Therefore, it is suggested in^[146] that the spin correlation function should be cut off at the mean free path but the Born approximation be retained formally. In this approach, the scattering by spins should give rise to a resistivity maximum at $T > T_c$ and the amplitude of this maximum should rise with decreasing electron momentum k . The scattering is analyzed in the Born approximation in^[147] using a spin correlation function with a weaker singularity in the range of short wave vectors than that represented by Eq. (3.7). It is concluded that, if the electron momentum k is low, the resistivity has a maximum at T_c . The electronic damping is not considered in^[146, 147].

Going outside the Born approximation is a difficult process in itself and it raises an additional problem: information is needed on the higher spin correlation functions and this is not yet available. Calculations of these functions are reported in^[93]. In contrast to the approach adopted in^[146-147], the zeroth-approximation states are not plane waves with a fixed direction of spin but plane waves with a fluctuating spin which becomes aligned to the local moment (Sec. c). This circumstance reduces considerably the scattering of electrons by long-wavelength fluctuations so that the transport relaxation time τ_k^C and the carrier lifetime both remain finite at T_c . The lower limit of the relaxation time is estimated using Eqs. (3.5)–(3.7) in the limit $\kappa \rightarrow 0$ and splitting four-spin correlation functions into two-spin forms:

$$\frac{1}{\tau_k^C} < 0.04 |B| \left(\frac{ASa}{|B|r_1} \right)^{4/3}. \quad (3.11)$$

However, such splitting is insufficient to establish whether the scattering process is strongest at T_c .

If $AS = 0.5$ eV, $W = 12|B| = 5$ eV, $r_1 \sim a$, the mobility at T_c due to the scattering by critical fluctuations should, according to Eq. (3.11), be at least several tens of the conventional units ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{sec}^{-1}$), which is in agreement with the experimental data for EuO, plotted in Fig. 8.

Defects may give rise to a peak of the resistivity ρ not only due to a change in the carrier density (Sec. e in Chap. 3), but also due to the scattering by magnetic moments in the vicinity of nonionized donors, which are

largest in the region of T_c (see Sec. e in Chap. 3). This scattering mechanism was first pointed out in^[120] and the calculations were carried out in^[144] on the assumption that the radius R of a ferromagnetic microregion ($R \geq a$). Even in the Born approximation the probability of scattering by such a magnetic cluster as a whole is $4\pi R^3/3a^3$ times greater than by individual atoms in the cluster (for $R \sim 2a-3a$, the increase is a factor of 50–100). The intensity of scattering rises particularly strongly in that range of T where a cluster gives rise to a virtual level near the bottom of the conduction band. Under certain conditions, electrons may even be captured by a cluster of this kind.

The Hamiltonians (2.3), (2.4), and (3.3) have been used to calculate the spontaneous Hall and Nernst coefficients^[148, 149] and the thermoelectric power α allowing for the drag of electrons by magnons.^[150] In the range $T \ll T_c/S$, the latter effect is weak because of the cutoff of the interaction between electrons and long-wavelength magnons, but at temperatures $T_c > T > T_c/S$ ($2S \gg 1$) it may be considerable (the drag thermoelectric power is $\alpha \propto T^{-2}$ for a nondegenerate ferromagnetic semiconductor and $\alpha \propto T^{-1}$ for a degenerate one). Thus, the value of α should have a maximum at $T \sim T_c/S$. If $T \ll T_c/S$, we may observe an additional maximum of α : this range is dominated by the drag of electrons by phonons and it passes through a maximum because of the scattering of phonons by the boundaries of a sample.

4. NONDEGENERATE ANTIFERROMAGNETIC SEMICONDUCTORS

a) Electrical and Optical Properties

The properties of antiferromagnetic semiconductors are in many respects different from those of ferromagnetic semiconductors. Above all, typical antiferromagnetic semiconductors do not exhibit the giant red shift of the absorption edge E_g . For example, the blue shift exhibited by EuTe ($E_g = 2.0$ eV) is only 0.03 eV and the magnetic field reduces it. In fields $H > 60$ kOe, the sign of this shift is reversed. The influence of a field H on the edge shift is strongest at T_N .^[6] The blue shift of CoO and MnS reaches 0.15 eV.^[236]

According to Eqs. (3.2) and (4.2) and estimates of the position of the bottom of the conduction band in the limit $T \rightarrow \infty$ (Secs. b and c in Chap. 3), a small blue shift corresponds to wide bands and a large one to narrow bands ($W \ll AS$), where $W \sim 0.5$ eV for CoO and MnS. However, a giant red shift is exhibited by metamagnets (for example, EuSe, see Fig. 2). For HgCr_2S_4 with a helicoidal order, this shift amounts to 0.4 eV,^[161] i.e., it is greater than for many ferromagnetic semiconductors. This observation confirms that the electron energy is governed not by the average but by the local magnetic moment of a crystal (Sec. c in Chap. 3). According to Eq. (3.2), the shift in a helicoidal material should be observed for $W \gg AS$ if $q < q_0$ since then the bottom of the conduction band descends when the temperature is lowered. If $W \ll AS$, bearing in mind that in the limit $T \rightarrow \infty$ the band width is $\sqrt{2}$ times less than in the ferromagnetic case (Sec. b in Chap. 3), we find from Eq. (3.2) that the inequality $qa < 1$ (q is the helicoid vector) is sufficient for the observation of the red shift. The edge of MnO shifts monotonically when the temperature is lowered.^[236]

A resistivity peak at the critical point, typical of ferromagnetic semiconductors, is not usually observed for antiferromagnetic semiconductors. The curve $\rho(T)$ frequently has a kink and this applies, for example, to EuFe .^[151] The activation energy of conduction of some nondegenerate antiferromagnetic semiconductors changes at the Néel point in such a way that at $T < T_N$ it is lower than at $T > T_N$ ^[154, 155] (for example, for MnTe_2 this energy is 0.011 eV at $T < T_N$ and 0.039 eV at $T > T_N$ ^[154]). A similar temperature dependence is exhibited also by the photoconductivity of EuTe (Fig. 6): it rises with temperature both below and above T_N , whereas at T_N its activation energy rises suddenly from 2.9×10^{-4} to 3.7×10^{-3} eV.^[6] However, it is not clear whether this sudden increase in the activation energy at T_N is a general rule.

In some cases, a resistivity maximum is observed at T_N . Evidently, as in the case of ferromagnetic semiconductors, it is due to lattice defects.

This explanation is confirmed by the results of direct experiments carried out on the degenerate antiferromagnetic semiconductor MnTe_2 .^[153] according to which relatively lightly doped crystals exhibit a singularity of $d\rho/dT$ at the Néel point and this singularity is similar to that of the specific heat. In the case of very heavily doped crystals, this singularity changes to a resistivity maximum in the vicinity of T_N (Fig. 10). However, the photosensitivity minimum of EuSe near T_N (compare Figs. 6 and 13) cannot be explained by the behavior of the resistivity (Sec. a in Chap. 6).

Some antiferromagnetic semiconductors (for example, NiO) are highly conducting only if they are heavily doped. It is usual to attribute this to the small width W of the carrier energy bands. In principle, W can be small compared with the energy of polarization E_p of the lattice by an electron. Then, a carrier is a small-radius polaron whose mobility rises exponentially with temperature.^[55-58] An attempt has been made to use this circumstance in explaining the experimental results^[59] showing that the mobility of holes in NiO is activated.

However, simple considerations show that the conditions for the appearance of small-radius polarons in magnetic semiconductors are fairly stringent and they certainly cannot appear in perfect NiO crystals with $T_N = 520^\circ\text{K}$. In fact, even in crystals with the maximum degree of ionicity (KCl , NaCl), the value of E_p does not exceed 0.2 eV,^[60] whereas in crystals with lower degrees of ionicity (particularly in magnetic semiconductors) this energy is even less. Since T_N is a quadratic function and W is a linear function of the small overlap of the d orbits, we have the inequality $T_N \ll W$. The chain of inequalities $T_N \ll W \ll E_p$ then shows that small-radius polarons may exist only at $T_N \ll 100^\circ\text{K}$ and the inequality $W \ll 0.1$ eV should be satisfied. In defect crystals, polarons can appear more easily because

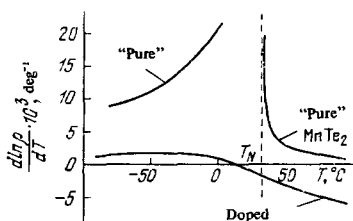


FIG. 10. Dependences of $d\rho/dT$ on T exhibited by "pure" and doped MnTe_2 crystals.

of fluctuations of the potential which tend to localize a carrier. Nevertheless, the latest experimental evidence shows that small-radius polarons are not formed in NiO .^[61, 63, 156]

There has been as yet no explanation of the change of the sign of the Hall effect in NiO after passing through T_N , as a result of which the sign in the paramagnetic region is opposite to the sign of the thermoelectric power.^[62]

b) Carriers in Antiferromagnetic Semiconductors with Narrow Bands

According to Eq. (3.2), the carriers in antiferromagnetic semiconductors with wide bands $W \gg AS$ can be assumed quite accurately to be ordinary band electrons. However, the situation is quite different in the case of narrow bands. Then, the state of a carrier at low temperatures can be described using the Hamiltonians (2.5) and (2.6).

We shall first consider the case $A < 0$.^[73, 157-159] Applying the equivalence of the s-d model with $S = 1/2$ and the Hubbard model,^[43] we shall give a qualitative explanation on the basis of this model (this model was used initially in^[157]) (Fig. 11).

We shall assume that initially a carrier (an excess electron) is located at an atom (0, 0) and the antiferromagnetic order in a crystal is retained (Fig. 11a). The excess electron may be transferred to a neighboring atom but only with a spin antiparallel to the spin of that atom. Consequently, the atom (0, 0) just left by the electron has a spin opposite to that which will be observed in the antiferromagnetic order (this atom is encircled in Fig. 11b). In terms of the s-d model, we can say that a magnon is created at (0, 0). Similarly, when an excess electron is transferred from (1, 0) to (2, 0), the spin of the (1, 0) atom becomes reversed (Fig. 11c). Each such spin reversal increases the energy of the system: the increase due to the first reversal is $(z-1)|I|S$, whereas the second and subsequent reversals increase the energy by $(z-2)|I|S$.

Thus, the spins of all the atoms traversed by an excess electron are reversed and the number of reverted spins increases with the number of steps in the trajectory of this electron. Moreover, the magnetic energy of the system increases proportionally. These effects are destroyed by the return motion of the excess electron. The situation is equivalent to the existence of a quasi-elastic force tending to return the electron to the (0, 0) atom. Consequently, an excess electron should oscillate around the central atom (0, 0). The existence of closed trajectories makes possible a translational motion of the excess electron since it may store the original spins without following exactly the original trajectory in the return journey. The same result is obtained by allow-

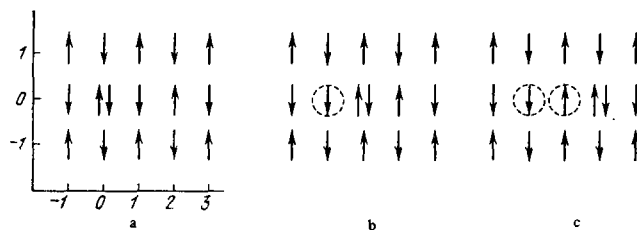


FIG. 11. Quasioscillator in the $A < 0$ case.

ance for zero-point spin oscillations.^[158, 159] This means that the equilibrium position of an electron also moves along a crystal so that the motion of an electron is similar to the motion of a pendulum with a moving point of suspension.

This state of a carrier is known as a quasioscillator.^[157] This is a new state of a carrier, which differs from the polaron state because the degree of deformation of the periodic structure oscillates with the electron around an equilibrium position.

The determination of the ground state of a system described by the Hamiltonian (2.6) is a very difficult mathematical problem even if this Hamiltonian is simplified by assuming approximately that \mathcal{H}_M is equal to $|I|S(z-2)\sum_g b_g^* b_g$. An upper limit of this energy can be obtained by considering only the trajectory of an electron with a finite number of steps away from the central atom. Trajectories with not more than three steps are considered in^[157] and it is found that

$$E < -3.7\beta + 11|I|S, \quad \beta = \frac{\sqrt{2S}|B|}{2S+1}. \quad (4.1)$$

A lower limit of the energy is also obtained in^[157]. A more general solution is given in^[158, 159, 73]. The energy band of a quasioscillator is very narrow (the width is of the same order as that of the magnon band).

The analogous problem is considered in^[97, 98, 160] using the Hubbard model. However, only the moments of the electron density of states are calculated and the quasielastic forces resulting from the spin reversal are ignored.

The situation is quite different if $A > 0$. In this case, it follows from Eq. (2.5) that the transfer of an electron to a neighboring atom produces a spin deviation not at the atom left by the electron but at the atom where it has arrived. Let us assume that the projection of the spin of an atom I is S and that of a neighboring atom II is $-S$ and that initially an electron with $\sigma = 1/2$ is located at the atom I (Fig. 12a). Then the total spin of this atom S_t , which is $S + 1/2$, is directed exactly upward. After the transfer of that electron to the atom I (Fig. 12b), the atom I is still directed exactly upward whereas the spin of the atom II deviates from the downward direction: the total spin of the atom II is $S + 1/2$ and its projection, because of the conservation of the spin projections of the whole system after the electron transition, is $-S + 1/2$.

The return transition of the electron restores the spin of the atom II. However, this happens also if the electron is transferred from the atom II not to the atom I but to another nearby neighbor whose spin is parallel to the spin of I. Thus, a simplified mechanism of the motion of a carrier in a crystal is as follows. The electron spin in atoms of the sublattice I is parallel to the sublattice moment. The transfer of an electron to an atom in the sublattice II is accompanied by the creation of a magnon in this sublattice and annihilation of a magnon when the

electron returns to the sublattice I. The energy used to create a magnon can be ignored because $|I|S^2 \ll B$. Therefore, the energy spectrum of a carrier subject to Eq. (2.5) is given by a dispersion law of the (3.1) type but with the band width reduced by a factor $\sqrt{2S+1}$:

$$E_k = \frac{zB\gamma_k}{\sqrt{2S+1}}. \quad (4.2)$$

A more rigorous analysis should allow for the fact that, in addition to the transitions from the atom II to the atom I accompanied by the recovery of the spin, we can also have transitions which leave a net spin deviation at the atom II and induce a deviation at the atom I. Such transitions result in the superposition on the motion of carriers of oscillations of the same type as in the $A < 0$ case. However, their role is now much less important: they increase the effective mass of a carrier by not more than 25%.^[73, 158, 159] The carrier spectrum is doubly degenerate because the electron spin can be parallel not to the sublattice I but to the sublattice II.

Thus, the participation of magnons in the motion of a carrier across a crystal makes the carrier spectrum of an antiferromagnetic semiconductor quite different from that obtained on the assumption that the spins of magnetic atoms are immobile, i.e., from that obtained from Eq. (2.2). In particular, if $A > 0$ and realistic values of the spin are assumed, the effective mass of a quasiparticle (quasioscillator) is only $\sqrt{2S+1}$ times greater than that of a band electron. An antiferromagnetic semiconductor can also have carrier states of quite different type, discussed in Sec. a, Chap. 6.

5. INFLUENCE OF INDIRECT EXCHANGE ON MAGNETIC ORDER IN MAGNETIC SEMICONDUCTORS

a) Indirect Exchange in Ferromagnetic Semiconductors and Photoferromagnetic Effect

Indirect exchange between magnetic atoms via conduction electrons is important in heavily doped magnetic semiconductors. For example, it has been found experimentally that an increase in the number of carriers in EuO and EuS can double the value of T_c .^[9, 112, 125, 165] The special feature of the indirect exchange in magnetic semiconductors is that it cannot be described by the effective Heisenberg Hamiltonian. This is a direct consequence of the low carrier density n , as a result of which the Fermi energy of carriers is $\mu \lesssim AS$ even in wide-band semiconductors (for example, if $m^* = 10^{-27} g$, $AS = 0.5$ eV, this energy μ reaches AS only for $n = 10^{21} \text{ cm}^{-3}$). In fact, the Hamiltonian $\mathcal{H}_A + \mathcal{H}_B$ of Eq. (2.1), which is linear in the d spins, can be used to find the effective Heisenberg Hamiltonian, which is a quadratic function of the spins, only in the second order of the perturbation theory in \mathcal{H}_A . The small parameter is AS/μ . This is the method used to derive the effective Heisenberg Hamiltonian in the indirect exchange energy theory developed by Ruderman, Kittel, Kasuya, and Yosida, which we shall abbreviate to RKKY theory (see, for example,^[54]).

In some investigations (see, for example,^[167, 168]), the RKKY theory is applied not only to degenerate but also nondegenerate magnetic semiconductors. It would seem that this may be justified by the smallness of the ratio $ASn/\mu N$ for degenerate magnetic semiconductors and of ASn/TN for nondegenerate materials ($N = a^3$). However, this is incorrect, as demonstrated by an analysis of the

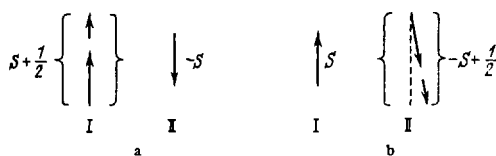


FIG. 12. Quasioscillator in the $A > 0$ case.

terms which are of higher orders in \mathcal{H}_A . The magnetic Hamiltonian in the RKKY theory is the correction to the electron energy due to the s-d exchange. Since each s electron interacts with d spins independently of other electrons, terms proportional to the number of nondegenerate electrons occur in the corrections of any order in \mathcal{H}_A to the energy of such electrons. Therefore, n does not occur in the ratio of the correction of the next order to the correction of the lower order in the limit $n \rightarrow 0$ and, consequently, this quantity cannot ensure that the ratio is small.

We can show that the parameter of the expansion applicable to a degenerate gas is AS/μ on the basis of the following considerations. If the average magnetization of a crystal \bar{S}_0 does not vanish, the Hamiltonian \mathcal{H}_A contains terms diagonal in respect of electrons and these may be included formally in the zeroth-approximation Hamiltonian. The energy corresponding to this Hamiltonian is

$$E_0 = \sum_{k\sigma} E_{k\sigma} n(\mu - E_{k\sigma}), \quad E_{k\sigma} = E_k - AS_0\sigma \quad (\bar{S}_0 \leq S). \quad (5.1)$$

The energy E_0 reduces to an expression which is quadratic in respect of the spins (i.e., in respect of \bar{S}_0) only if the distribution function $n(\mu - E_{k\sigma})$ can be expanded in terms of AS_0/μ for any magnetization subject to the condition $\bar{S}_0 \leq S$. Similar considerations demonstrate that the RKKY theory applies to nondegenerate magnetic semiconductors only if $AS/T \ll 1$. It should be noted that at 100°K the parameter in this inequality is ~ 100 .

The inapplicability of the RKKY theory to the $\mu < AS$ case can be demonstrated also qualitatively by considering the ferromagnetic order at $T = 0$. Electrons are then fully spin-polarized and this state differs radically from the ground state of free electrons described by the Hamiltonian \mathcal{H}_B of Eq. (2.1) because the electrons are not spin-polarized. This means that the former state cannot be obtained from the latter in any order of the perturbation theory which is finite in respect to \mathcal{H}_A .

The approach developed below differs from the RKKY theory because a considerable proportion of the s-d exchange is included in the zeroth-approximation Hamiltonian and this part of the exchange is not expanded.

The magnon spectrum of a strongly degenerate ferromagnetic semiconductor is readily established in the main approximation with respect to $1/2S$ using Eqs. (2.3), (2.4), and (3.3)^[70, 166, 89] averaged over electrons allowing for the smallness of $k_F = \sqrt{2m^* \mu}$:

$$\omega_q = \omega_q^0 + \frac{Avq^2}{2(q_0^2 + q^2)} \quad \text{for } W \gg AS > \mu, \quad (5.2a)$$

$$\omega_q \approx \omega_q^0 + \frac{z|B|\nu}{2S}(1 - \nu_q) \quad \text{for } W \ll AS, \quad (5.2b)$$

where ω_q^0 is the magnon frequency in the absence of indirect exchange in Eq. (2.1), $\nu = n/N$ is the number of s electrons per magnetic atom, and $q_0^2 = 2m^*AS$.

It is clear from Eq. (5.2a) that the nonanalyticity of this result in respect of AS/W (q_0^2 occurs in the denominator) is of basic importance. Both Eqs. (5.2a) and (5.2b) satisfy the requirement associated with the isotropy of the system: in the limit $q \rightarrow 0$, the magnon frequency is proportional to q^2 , i.e., the $T^{3/2}$ law describes the temperature dependence of the magnetization.

At first sight, it might appear strange that the magnon frequency of Eq. (5.2b) is independent of the s-d exchange constant A although the indirect exchange is a consequence of the s-d exchange. However, the s-d ex-

change cannot, by itself, give rise to the indirect exchange if an electron is permanently located at some atom and cannot travel to neighboring atoms. Therefore, if $B = 0$, the contribution of electrons to the magnon frequency should vanish, which is reflected in Eq. (5.2b). The s-d exchange integral drops out of this equation because of the spin-polaron state of an electron: its spin is rigidly linked to the local moment no matter how far the latter deviates from the total moment of the crystal. For this reason, the integral drops out also from Eq. (5.2a) if $q^2 \ll q_0^2$ and then Eq. (5.2a) reduces to (5.2b).

It follows from Eqs. (5.2a) and (5.2b) that the effective exchange integral $J_{\text{eff}}(\mathbf{g}) = -(1/N) \sum_{\mathbf{q}} \omega_{\mathbf{q}} e^{-i(\mathbf{q} \cdot \mathbf{g})}$ for $E \ll AS$ does not vanish only for the nearest neighbors, whereas for $W \gg AS$ it decreases exponentially at a distance q_0^{-1} . This integral does not exhibit any Ruderman-Kittel oscillations.

The magnon frequency increases with increasing ν in the $\nu \ll 1$ range, i.e., conduction electrons tend (as expected) to maintain a ferromagnetic order. Since T_C is comparable with the magnetic ordering energy (per atom), conduction electrons shift the Curie point of a doped crystal by an amount $\Delta T_C \approx AS\nu/2$ if $\mu \ll AS \ll W$ and by $\sim z|B|\nu$ if $W \gg AS$. The correctness of these orders of magnitude is confirmed by the data on EuO^[112] if we assume that $AS/2$ is 0.25 eV, deduced from the red shift.^[6] For example, if $n \sim 5 \times 10^{19} \text{ cm}^{-3}$, the shift of the Curie point ΔT_C is 10°K ($\sim 10^{-3}$ eV)^[112] and the value of $AS\nu/2$ is 1.6×10^{-3} eV.

As in the case of extrinsic nondegenerate ferromagnetic semiconductors, the paramagnetic Curie temperature Θ of degenerate ferromagnetic semiconductors should exceed T_C . However, the cause is now different: it is the non-Heisenberg nature of the direct exchange via conduction electrons. If the inequality $\sqrt{W\mu} \gg AS$ is satisfied, which ensures that the electron damping is small in the range $T \gg T_C$,^[93] we can calculate Θ using the expression (5.1). Since Θ is defined for weak magnetizations \bar{S}_0 , it can be expanded in terms of AS_0/μ . Formally, this gives the RKKY results in the $W \gg \mu$ limit: the shift of Θ is $A^2S(S+1)\nu\mu^{-1}/8$, i.e., it is $\sim AS/\mu$ times greater than ΔT_C . In contrast to the shift of Θ due to magnetic quasimolecules in nondegenerate ferromagnetic semiconductors (Sec. d in Chap. 3), this shift is now independent of T , i.e., the Curie-Weiss law should be satisfied. When n is increased, the difference between the shifts of Θ and T_C should decrease, i.e., the value of $\Theta - T_C$ should pass through a maximum.

This effect is exhibited by $\text{Eu}_{1-x}\text{Gd}_x\text{S}$, for which the difference between Θ and T_C is practically zero for $x = 0$ but reaches 20°K for $x \sim 0.01$; however, when x is increased still further, the difference decreases.^[9] According to^[130], the value of Θ of $\text{Eu}_{1-x}\text{Gd}_x\text{O}$ exceeds T_C both for $0 < x < 0.015$, when the conductivity is very low, and for $x \geq 0.015$ when this crystal behaves as a semimetal. In the former case, there are deviations from the Curie-Weiss law but not in the latter case, which is in agreement with the above theory. The value of Θ is close to T_C when x is large.

The indirect exchange on the surface of a ferromagnetic semiconductor is different from the bulk effect because the surface is charged relative to the bulk. The surface charge may be due to the presence of surface electron levels, adsorption, etc., and due to the application of an external electric field. Consequently, the sur-

face magnetization is different from the bulk value. The magnon spectrum has a branch of quasisurface magnons, which oscillate within the surface-charge layer and are damped outside it; moreover, in contrast to true surface magnons, the surface itself may be classically unattainable for quasisurface magnons. [166, 170]

The influence of the indirect exchange on the surface magnetization of a ferromagnetic semiconductor is supported by the experimental results available on EuO. [152, 171] The neutron and photoelectron polarization indicates that the surface magnetization is much lower than the bulk value and this is true even at temperatures much lower than the Curie point. It is clearly due to a weakening of the direct exchange.

Crystals containing a few percent of Gd or La exhibit a surface magnetization much higher than pure crystals, which is evidence of the enhancement of the ferromagnetic coupling on the surface via conduction electrons resulting from doping. The surface paramagnetism is destroyed also by the chemisorption of Cs on EuO. [233] This can be explained by assuming that adsorbed Cs atoms behave as surface donors. Their valence electrons are drawn into the crystal and they join the collective state, being still concentrated near the surface. Therefore, they participate in the indirect ferromagnetic exchange between surface ions of Eu.

It is suggested in [167, 168] that illumination of a magnetic semiconductor should, because of the indirect exchange via photoelectrons, increase T_C of ferromagnetic semiconductors and convert antiferromagnetic semiconductors to the ferromagnetic state. However, the application of the RKKY theory results in an underestimate of the necessary photoelectron densities by 2–3 orders of magnitude (according to [167], the value of T_C should increase by 100°K for $n \sim 10^{17} \text{ cm}^{-3}$, whereas, according to the data given in the present section, such a rise of T_C requires $n \sim 10^{20} - 10^{21} \text{ cm}^{-3}$). In practice, it is hardly possible to generate a photoelectron density exceeding $10^{17} - 10^{18} \text{ cm}^{-3}$ and this is why the effect has not been observed experimentally. (It is reported in [234] that CdCr₂Se₄ exhibits the reverse effect.)

It is reported in [169] that illumination reduces the high-frequency magnetic susceptibility of CdCr₂Se₄ (frequency $\sim 2 \text{ MHz}$) below T_C and the reduction disappears at $T > T_C$. This photoferromagnetic effect is not due to heating because heating increases the susceptibility. The maximum of the spectral characteristic of the effect (Fig. 9) coincides with the photoconductivity maximum observed at $T < T_C$ and the relaxation times ($\sim 10^{-2} - 10^{-3} \text{ sec}$) of the two phenomena are the same. Doping of this material with Ga does not alter the spectral characteristic. In the presence of 0.1% Ga, the effect reaches its maximum value exceeding by an order of magnitude the value for a pure crystal. [140] Clearly, the photoferromagnetic effect has a specific dynamic nature and this explains its high value in the presence of relatively few photoelectrons ($\sim 10^{15} \text{ cm}^{-3}$). It resembles the strong influence of photoelectrons on the dynamic plasticity of crystals and the negligible influence on the static plasticity. [46]

b) Heavily Doped Antiferromagnetic Semiconductors and Cantèd Antiferromagnetism

A particularly interesting situation arises when an antiferromagnetic semiconductor is heavily doped: the indirect exchange via conduction electrons, which tends

to establish a ferromagnetic order, competes with the direct exchange via magnetic atoms, tending to establish an antiferromagnetic order. Naturally, at sufficiently high conduction electron densities which ensure the predominance of the indirect exchange, a ferromagnetic order should be established. This is observed, for example, in MnTe when the hole density reaches 10^{21} cm^{-3} . [172] In metamagnets, a ferromagnetic order is established at anomalously low carrier densities. This makes it possible to induce the ferromagnetic state in these materials by illumination. This question is considered in [235] applying a variational principle (formulated in that paper) to phase transitions under nonequilibrium conditions.

Even if the carrier density is insufficient for the establishment of a ferromagnetic order, the properties of heavily doped antiferromagnetic semiconductors differ considerably from those of Heisenberg antiferromagnets. This is manifested particularly by the anomalous dependence of the moment of a crystal on an external magnetic field at $T = 0$. In the wide-band case, this dependence is found by minimizing the energy with respect to the moment $M = S \cos \theta$, where θ is the angle between field and the sublattice moment, $2S \gg 1$. [173, 174]

$$J_{\text{eff}}(M) \equiv J + \frac{P_{\pi} - P_0}{2} = -\frac{HS}{2M}, \quad J = zIS, \quad (5.3)$$

$$P_0 = \frac{AS}{2M} (\nu_{\uparrow} - \nu_{\downarrow}), \quad P_{\pi} \approx \frac{4S}{2W} (\nu_{\uparrow} + \nu_{\downarrow})_a, \quad \nu_{\sigma} = \frac{n_{\sigma}}{N},$$

where ν_{σ} is the number of electrons with a spin projection σ per atom. Clearly, in the limit $\mu \gg AS$, the value of J_{eff} reduces to the usual Heisenberg effective exchange integral, which is independent of M , and Eq. (5.3) represents the usual condition for the equilibrium of a Heisenberg antiferromagnet in a magnetic field. However, if $\mu \lesssim AS$, the dependence of J_{eff} on M is strong.

It is thus found that the initial magnetic susceptibility χ_0 of a doped antiferromagnet is $A\Phi B [1 - (3A^2S\nu/16\mu |J|)]^{-1}$ times higher than of an undoped antiferromagnet ($\nu = \nu_{\uparrow} + \nu_{\downarrow} = n/N$). The total polarization of electrons is achieved in relatively weak external fields because the electron spins experience the induced (by the same electrons) molecular field $AM/2$ which exceeds the external field by a factor $A_{\chi}/2 \sim AS/T_N$, i.e., by several orders of magnitude (the giant Zeeman effect in antiferromagnetic semiconductors is described in [173]). As the field H increases, the susceptibility χ decreases, and when all the electrons become spin-polarized, the susceptibility assumes the same value as that of an undoped antiferromagnet. The sublattice collapse field H_F is $1 - (AS\nu/4|J|)$ times lower than the corresponding field for a pure antiferromagnet. (The behavior of χ is shown qualitatively in Fig. 15b.)

If the Fermi surface is sharply defined, the magnetic susceptibility of a crystal should oscillate with the field. These oscillations are quite different from the de Haas–van Alphen oscillations and the former are associated with the redistribution of electrons between the Zeeman subbands and not between the Landau subbands. These oscillations disappear when the electrons become totally spin-polarized. [173]

Equation (5.3) has nontrivial solutions $0 < M_0 < S$ in a certain range of electron densities $\nu_A < \nu < \nu_F$ even in the absence of an external field. The left-hand limit ν_A is found from the condition $\bar{J}_{\text{eff}}(0) = 0$, i.e., from the condition that $\chi_0(\nu_A)$ becomes infinite. The right-hand limit ν_F , found from $\bar{J}_{\text{eff}}(S) = 0$, corresponds to vanish-

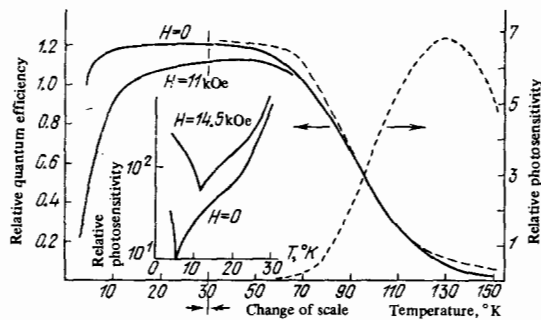


FIG. 13. Luminescence of EuSe (inset shows the photosensitivity of EuSe).

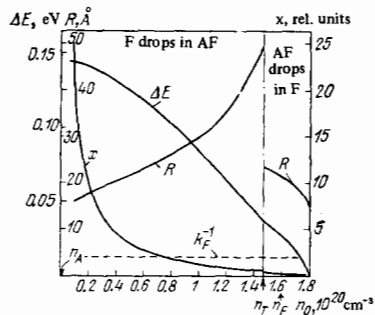


FIG. 14. Collective ferron state in a degenerate antiferromagnetic semiconductor. Here, F denotes ferromagnet or ferromagnetic and AF denotes antiferromagnet or antiferromagnetic.

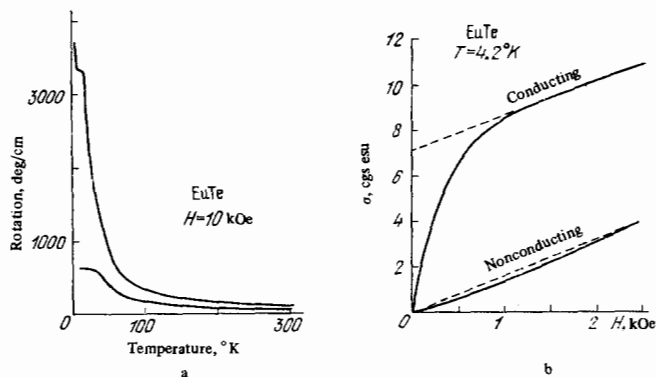


FIG. 15. Faraday rotation in degenerate (upper curve) and nondegenerate (lower curve) EuTe (a) and dependence of the magnetization on the field in degenerate and pure EuTe (b).

ing of the collapse field (soft antiferromagnetic and ferromagnetic magnon modes appear at ν_A and ν_F , respectively). If $AS/\mu < 1$, the width of this interval increases with the parameter AS/μ in accordance with the law

$$\nu_F = \frac{4|J|}{A} = \frac{3}{4} \nu_A \frac{AS}{\mu(\nu_A)}, \quad (5.4)$$

$$\mu(\nu_A) = \frac{(3\pi^2 n_A)^{2/3}}{2m^*} \quad (n_A = \nu_A N).$$

In the limit $\mu/AS \rightarrow \infty$ (Heisenberg exchange), we find that $\nu_A \rightarrow \nu_F$, i.e., as ν increases, an antiferromagnetic order suddenly changes to a ferromagnetic one.

Thus, in the range $\nu_A < \nu < \nu_F$, energy considerations show that a canted antiferromagnetic order with the angle between the sublattice moments not exceeding π is preferred both for ferromagnets and antiferromagnets. Near ν_A the moment of a crystal increases with ν as $\sqrt{\nu - \nu_A}$ and then linearly. In contrast to the weak Dzyaloshinskii-Moriya weak ferromagnetism, which is due to the relativistic interactions, the possibility of a canted antiferromagnetic order is not restricted by the

symmetry properties of the system under consideration.

If the value of M_0 is low, the initial susceptibility of a canted magnetic material is proportional to M_0^2 , i.e., it increases on approach of ν to ν_A . When the moment is sufficiently large (i.e., when ν or H is sufficiently high), the susceptibility tends, as in the $\nu < \nu_A$ case, to the value for a pure crystal.

Similar properties are exhibited also by heavily doped narrow-band antiferromagnetic semiconductors and the possibility of a canted antiferromagnetic order in these materials was pointed out a long time ago by de Gennes.^[174] However, the analysis of this topic given by de Gennes^[174] is not quite correct because it is based on the use of the Hamiltonian (2.2) with $\tilde{\gamma}_{gg+\Delta} = 0$. It is incorrect to conclude that a canted antiferromagnetic order appears for any value of ν no matter how small [this conclusion is a consequence of the use of Eq. (2.2) in the $\theta_{gg+\Delta} = \pi$ case]. In plotting the phase diagram for $T \neq 0$, we cannot assume that, in all cases, we have $\tilde{\gamma}_{gg+\Delta} = 0$. A more correct analysis of this topic is made in^[73, 175, 174] for the case when the spin of an atom is antiparallel to the spins of its nearest neighbors, moreover, the values of ν_A and ν_F are found in these papers.

A canted antiferromagnetic order is preferred, for energy reasons, to ferromagnetic and collinear antiferromagnetic orders but this does not guarantee the stability of the canted configuration. Doubts about its stability appear if we investigate the magnon spectrum of a canted antiferromagnet in the $W \gg AS$ case.^[220] It is found that, if $\nu > 4\nu_A$, the frequencies of short-wavelength magnons become imaginary, i.e., we know that if $\nu_F > 4\nu_A$ there is a range of carrier densities in which a canted order is unstable. It is possible also that in the range $\nu < 4\nu_A$, where the magnon frequencies are real and positive, a canted antiferromagnetic order does not correspond to the absolute but to a relative energy minimum. Nevertheless, even then we may expect a different two-lattice substructure in the range $[\nu_A, \nu_F]$. This follows from the general theory of phase transitions^[221] since the approach to ν_F from the high-density side results first in vanishing of the frequency of magnons with $\mathbf{q} = \pi$. This follows from Eqs. (5.2a) and (5.2b) if the negative value of $\omega_{\mathbf{q}}^0$ is allowed for. This structure may be the one described in^[176]: the moment in one of the sublattices is less than in the other so that the antiferromagnetic vector is collinear to the magnetic moment ("ferromagnetic" structure).

The question of whether a single-sublattice unsaturated ferromagnetic order (with longitudinal components of the spins parallel in one direction and arbitrary transverse components) can be established in the range $[\nu_A, \nu_F]$ instead of a canted antiferromagnetic structure is considered in^[176]. If $W \ll AS$, a test wave function can be obtained to describe such a state. States of this kind are possible only in antiferromagnetic semiconductors with large numbers of defects in which the damping of short-wavelength magnons is sufficiently strong. They are also possible in Pauli paramagnets which exhibit only a short-range antiferromagnetic order.^[174]

We must also point out that, on the surface of a heavily doped antiferromagnetic semiconductor with $\nu < \nu_A$, we can produce a layer with nonzero magnetization by increasing the carrier density to the value exceeding ν_A .^[166]

In analyzing the experimental results, we must bear in mind that the above anomalies of magnetic properties of heavily doped antiferromagnetic semiconductors may not be due to a canted structure but to other factors (Sec. b in Chap. 6). Clearly, this is true of n-type EuTe (Fig. 15) investigated in^[38]. A canted structure may be formed in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ crystals in which an increase in x causes an antiferromagnetic order to transform to a ferromagnetic one and reduces strongly the value of ρ . Neutron-diffraction spectra of these crystals show that, in a certain range of x , they are superpositions of spectra corresponding to ferromagnetic and antiferromagnetic configurations,^[177] which may be true of a canted structure^[74] or another type of two-sublattice structure with a nonzero moment.

An unsaturated ferromagnet is obtained when FeS_2 and NiS_2 crystals (Pauli paramagnets) are doped with cobalt. As the cobalt concentration is increased, the spontaneous moment of a crystal rises and the moment per atom, deduced from the paramagnetic susceptibility, is equal to the spin of isolated magnetic ions. Doping also increases considerably the conductivity.^[178] These results are in qualitative agreement with the theory in^[176].

6. FERRON STATES IN NONDEGENERATE AND DEGENERATE SEMICONDUCTORS. RESISTANCE OF DEGENERATE SEMICONDUCTORS

a) Individual Ferron States

As pointed out in Chap. 5, conduction electrons tend to establish and maintain a ferromagnetic order in a crystal because this order ensures minimum electron energy [see, for example, Eq. (3.2)]. For example, a ferromagnetic order should be established in an antiferromagnet at $T = 0$ if $\nu > \nu_F$ (Sec. b in Chap. 5). However, if ν is insufficiently high to establish ferromagnetism throughout the crystal, an energy gain can still be obtained if electrons are concentrated in some part of a crystal and ferromagnetism is established in that part. Thus, a single electron may establish a ferromagnetic microregion and may be self-localized in this region.^[194,195] The energy lost due to the reversal of the d spins is compensated by the gain in the electron energy because a ferromagnetic microregion is a potential well for electrons in an antiferromagnetic crystal. In principle, an electron together with its ferromagnetic region can move along a crystal, but under real conditions the mobility of such a system is very low and the system can be regarded as localized.

A complex formed from an electron and a microregion of the second phase, which is established by this electron, is a quasiparticle of a new type^[194,195] with properties quite different from those of a polaron. Such quasiparticles are destroyed at sufficiently high temperatures T but if the depth of the potential well is sufficient, they may exist even in the paramagnetic region.

At high temperatures, a ferromagnetic microregion may appear because of thermal fluctuations even in the absence of conduction electrons. It may happen that the number of fluctuations capable of capturing a conduction electron is large compared with the number of such electrons. Therefore, an electron does not have to generate a ferromagnetic microregion, i.e., localization of electrons in fluctuations of this type resembles the Anderson localization in nonperiodic structures (glasses,

etc.). The capture of an electron by thermal fluctuations is possible only in antiferromagnets but also in ferromagnets, as pointed out first in^[201]. Clearly, the conditions for self-localization are easier to satisfy in such fluctuations than the Anderson localization conditions. Further studies of the self-localization of electrons in ferromagnetic regions are reported in^[202-209]. Such states will be called individual ferrons.

Collective ferron states are possible in degenerate magnetic semiconductors when the appearance or an increase in the degree of a ferromagnetic order in some part of a crystal occurs as a result of an increase of the electron gas density as a whole.^[46,196,197] A reduction in the electron energy as a result of a simultaneous establishment of a ferromagnetic order by these electrons is equivalent to the existence of a specific mechanism of attraction between electrons.

Calculations of individual ferron states in an antiferromagnet at $T = 0$ are carried out in^[194,196] by a variational method. It is assumed that the full ferromagnetic order is established in a microregion of radius R and that, outside this region, the ideal antiferromagnetic order is retained. The depth of a ferromagnetic potential well in the $A > 0$ case is

$$U = \frac{1}{2} AS \text{ for } W \gg AS, \quad U = \frac{1}{2} W [1 - (2S + 1)^{1/2}] \text{ for } W \ll AS, \quad (6.1)$$

and, in the latter case, the effective mass of a carrier inside a ferromagnetic region is $\sqrt{2S + 1}$ times smaller than outside this region [Eq. (4.2)]. The radius R is found from the minimum of the total energy of the system. It should exceed the minimum value R_m beginning from which an electron level appears in a well. If $R \gg a$ and $AS \ll W$, R_m is given by the usual expression^[75] but, if $AS \gg W$, it is given by a slightly modified formula because of the difference between the effective masses in the ferromagnetic and antiferromagnetic regions:

$$R_m = \frac{\pi}{2} a \sqrt{\frac{2|B|}{AS}} \quad \text{for } AS \ll W, \quad (6.2)$$

$$R_m = \frac{\pi}{2} a [z(\sqrt{2S+1}-1)]^{-1/2} \quad \text{for } AS \gg W,$$

and the energy is found from the equations (see^[75])

$$E = \frac{4\pi}{3} \left(\frac{R}{a}\right)^3 |J|S - |B| \left(z - \frac{a^2 k^2}{2}\right) - \frac{AS}{2}, \quad (6.3)$$

$$\frac{2}{\pi} k R_m = \sin k R \left(\frac{\pi}{2} < k R < \pi\right), \quad \frac{dE}{dR} = 0.$$

The solution of Eq. (6.3) can be obtained explicitly only for $R \gg R_m$:

$$E = -z|B| - \frac{AS}{2} + \frac{5}{3} \pi^{3/5} |B|^{3/5} |JS|^{2/5}, \quad (6.4)$$

$$R = a \left(\frac{\pi}{a} \left|\frac{B}{JS}\right|\right)^{1/5}.$$

The system (6.1)–(6.3) can be used to obtain the condition under which a ferron state is preferred for reasons of energy:

$$|J|S < 0.024U \left(\frac{a}{R_m}\right)^3. \quad (6.5)$$

It is worth noting that, according to Eq. (6.4), a full gain in the s-d exchange energy is obtained for ferrons of very large radius, irrespective of the value of AS/W . In this respect, the ferron states corresponding to $AS \ll W$ resemble spin-polaron states in which also a full s-d energy gain is obtained for large characteristic lengths of magnetic inhomogeneities (Sec. c in Chap. 3).

Self-localized electron states of a different kind are proposed in^[74]; in these states, the spin of one atom deviates from the direction of the moment in its sublattice and the angle generally does not reach π . For parameters typical of semiconductors, ferron states are much more preferable from the point of view of energy. Nevertheless, there is a definite interest in the case when the spin of one magnetic atom is directed opposite to the moment of its sublattice. An analysis^[70, 73] shows that the bound states of an electron with such a spin are possible only if $W \ll AS$ provided $S > 1$ and the result in^[74], based on Eq. (2.2), is valid only for $\sqrt{2S} \gg 1$ (this applies also to other investigations of ferrons in antiferromagnetic semiconductors with $W \ll AS$, such as those reported in^[206]).

For typical values of $AS/2W \approx 0.1$ and $W \approx 3$ eV, it follows from Eq. (6.5) that ferrons can exist in an antiferromagnetic semiconductor with $T_N \lesssim 15^\circ\text{K}$, for example, in EuTe. The radius of a ferromagnetic microregion amounts to 2–3 lattice constants, so that the ferron moment may reach hundreds of atomic moments.

In metamagnets, the magnetic energy needed to form a ferromagnetic microregion is very small and ferron states of much larger radius are possible. The situation is particularly interesting in EuSe, where—in addition to a ferromagnetic order—we can also have a ferrimagnetic order and the energy needed to produce the latter is even less (Fig. 1). In this case, ferrons are more complex: a ferromagnetic sphere of radius $R \approx 10$ a is surrounded by a ferrimagnetic shell of thickness $\sim(2-3)a$. The moment of such a quasiparticle may reach several thousands of atomic moments. Photoexcitation of ferrons may affect considerably the susceptibility χ of a crystal. In the $1.8^\circ\text{K} < T < 2.8^\circ\text{K}$ range, electrons may become self-localized in a ferromagnetic region inside a ferrimagnetic phase.^[198]

Ferron states in an antiferromagnet with $W \ll AS$ have the special property that, as S increases, the energy gain becomes greater. In a material with a band width $W \sim 0.5$ eV, ferrons may appear if $T_N \sim 40^\circ\text{K}$ for $S = 7/2$ and $T_N < 8^\circ\text{K}$ for $S = 1$. If $A < 0$, self-localized states are more complex^[199] because outside a ferromagnetic microregion a carrier behaves as a quasi-oscillator (Sec. b in Chap. 4) (the situation corresponding to $W \gg AS$, $A < 0$ is the same as for $A > 0$).

Ferrons are destroyed by strong magnetic fields and these fields are weaker than those needed for the collapse of the sublattice moments.^[200]

When the temperature is increased sufficiently, ferrons dissociate and, in principle, the dissociation temperature may exceed T_N . Conditions for the stability of ferrons at finite temperatures T are naturally governed not by the requirements that the total energy of the system should be minimal but the free energy should be minimal. If $AS \ll W$, the results represented by Eqs. (6.4) and (6.5) can be generalized in a trivial manner to the $T \gg T_N$ case. It is sufficient to replace the gain in the magnetic energy per atom $|J|S$ due to the creation of a ferromagnetic microregion with the gain in the free energy $T \ln(2S + 1)$. We can see from Eq. (6.5) that, for parameters typical of rare-earth compounds ($S = 7/2$, $AS/2W = 0.1$, $W = 3$ eV), ferrons may exist at $T \gg T_N$ provided $T_N \ll 10^\circ\text{K}$.

The problem of ferron states in narrow-band materials at finite temperatures is much more complex be-

cause the state of a carrier moving freely across a crystal is not known. A convincing solution of this problem has yet to be obtained. In very rough estimates, we may assume that, if $T \gg T_N$, free carriers move in a band of width $2z|B|\sqrt{(S+1)(2S+1)}$ ^[78] (Sec. b in Chap. 4). Then, Eq. (6.1) should be modified by replacing $\sqrt{2S+1}$ with $\sqrt{(2S+1)/(S+1)}$ and $|J|S$ in Eq. (6.3) should be replaced with $T \ln(2S+1)$.

Naturally, these estimates apply also to ferromagnetic semiconductors at temperatures $T \gg T_c$. In contrast to an antiferromagnetic semiconductor, ferron states in a ferromagnetic material may appear only at sufficiently high temperatures when a ferromagnetic order in a crystal is largely destroyed. However, we must bear in mind that, if $W \gg AS$, the s-d energy shift of a free electron is governed by the short-range rather than by the long-range order. The short-range order is destroyed at much higher temperatures than the long-range order and, therefore, even close to T_c the s-d shift is still fairly large. If $W \ll AS$, at temperatures close to T_c the bottom of the band again lies much lower than at $T \gg T_c$ (Secs. b and c in Chap. 3 and Figs. 2 and 3). This is a further difficulty impeding the formation of ferrons in a ferromagnetic semiconductor and it should be allowed for in the calculations (this has not yet been done). We may expect that, for the parameters given above, ferron states may appear in a wide-band ferromagnetic semiconductor at temperatures $T_c \ll 10^\circ\text{K}$, which is in agreement with^[206]. Thus, ferrons are much less likely to appear in ferromagnetic semiconductors than in antiferromagnetic materials. In particular, they cannot appear in EuS and EuO.

An analysis of the luminescence and photoconductivity of EuSe and EuTe led Wachter^[6] to the conclusion that ferron states should appear in these materials. Usually, a strong luminescence is attributed to the presence of defects which give rise to local levels in the electron spectrum. However, the luminescence of EuSe increases in strength with the purity of the crystal. In the temperature range $T \gg T_N$ the application of a magnetic field has little influence on the luminescence but at 4.2°K a field of 11 kOe, which produces a magnetization amounting to 80% of its maximum value, reduces the luminescence by a factor of 5 but enhances strongly the photoconductivity (Fig. 13). This shows that the magnetic field destroys the local levels involved in electron transitions in its absence. The levels which exist only at $T \lesssim T_N$, are not associated with defects, and which are destroyed by a magnetic field are the ferron levels.

It is suggested in^[201] that the sharp resistivity peak of EuO near T_c , which is typical of ferromagnetic semiconductors, is due to the capture of conduction electrons by magnetization fluctuations. This interpretation is not supported by the theoretical estimates given above or by the experimental observations showing that the amplitude of this peak depends strongly on the concentration of defects in a crystal and by the observation that the photoconductivity of very pure crystals shows no minimum near T_c (sec. e in Chap. 3). However, this effect can be explained by the combined influence on electrons of magnetization fluctuations and defects, as a result of which ferrons localized near these defects are formed on approach to T_c . Essentially, this is the situation considered earlier in Sec. d of Chap. 3, where a localized electron is assumed to increase the degree of ferromagnetic order in the vicinity of a defect.

b) Collective Ferron States and Localized Ferrons in Antiferromagnetic Semiconductors

In degenerate antiferromagnetic semiconductors, we may have not individual but collective ferron states so that a crystal splits into ferromagnetic and antiferromagnetic domains. In the former, the carrier density is higher and, in the latter, it is lower. Characteristic dimensions of ferromagnetic domains are considerably larger than the average distance between electrons, [46, 197]. Consequently, the energy required to form such domains (calculated per one electron) is considerably less than in the case of individual ferrons. On the other hand, in contrast to individual ferrons, formation of collective ferrons is accompanied by an increase in the Coulomb energy and in the kinetic energy of electrons. Therefore, the conditions for the appearance of collective ferrons are different than those for individual ferrons. In particular, such appearance depends strongly on the electron density.

Generally, the instability range of homogeneous states of a system does not agree with the interval $[n_A, n_F]$ of the canted order (Sec. b in Chap. 5). Moreover, an inhomogeneous state is possible even for $n > n_F$ when in a homogeneous state the whole crystal would have been ferromagnetic. The origin of this situation is as follows: electrons concentrated in ferromagnetic regions realize the full gain in the s-d exchange energy, in the same way as in a homogeneous state. However, the recovery of an antiferromagnetic order in the rest of the crystal results in a gain in the energy of direct exchange between magnetic atoms (it would be more correct to call these antiferron states).

Direct variational calculations are reported in [46, 197, 213] for heavily doped antiferromagnetic semiconductors with $\mu \gg e^2 n^{1/3} / \epsilon_0$, $W \gg AS$. It is assumed that the carrier density in ferromagnetic regions is independent of the coordinate and equal to zero in antiferromagnetic regions (this can be justified for typical parameters [46]). Three types of geometry are considered: 1) alternating ferromagnetic and antiferromagnetic planar layers; 2) ferromagnetic spheres forming a periodic structure inside an antiferromagnetic matrix; 3) antiferromagnetic spheres forming a periodic structure inside a ferromagnetic matrix.

The effective surface energy of the phase boundaries is the increase in the electron energy which occurs because only the part of space occupied by ferromagnetic regions is accessible to electrons. This can be found by expanding the density of electron states in terms of the reciprocal of the product of the Fermi momentum and the characteristic dimensions of the system (see, for example, [47]). It should be stressed that it would be a serious error to introduce a surface energy of the boundaries separating antiferromagnetic and ferromagnetic phases which would be independent of n : this would have no meaning because these phases cannot exist for $n = 0$. The total energy of a system of this kind can be represented by a sum of the bulk energy, given by the Thomas-Fermi approximation, and of the surface energy found as above.

An inhomogeneous state is preferred from the energy point of view if $a_B^{-3} \ll n \ll n_A$ and

$$\frac{AS}{2} > 2^{5/3} \left[\frac{2}{5} \mu_F + \left(\mu_F^2 \frac{e^4 n_F^{1/3}}{\epsilon_0} \right)^{1/3} \right], \quad \mu_F = \frac{(6\pi^2 n_F)^{2/3}}{2m^*}, \quad (6.6)$$

where a_B is the Bohr orbit radius in a crystal. If the

doping is heavy so that $a_B^{-3} \ll n_A < n_F$, the second term in Eq. (6.6) is less than the first and the condition (6.6) differs only by a factor of the order of unity from the condition of existence of individual ferrons given by Eq. (6.5). At low carrier densities, ferromagnetic spheres inside an antiferromagnetic matrix provide the most favorable configuration from the energy point of view; the radius of these spheres increases with n but the charge density decreases. Near n_F , the most favorable configuration from the energy point of view is represented by antiferromagnetic spheres in a ferromagnetic matrix. The radius of these spheres is greater than the average distance between electrons by a factor $\sim 2(n_F^{1/3} a_B)^{1/3}$.

At carrier densities n_T corresponding to the equalization of these two geometries, the ferromagnetic component of a crystal transforms from multiply connected to singly connected. Therefore, a sharp rise of the conductivity should occur when n is increased near n_T (in terms of the adopted approximation, this rise represents to an insulator-metal transition). The density n_T decreases with rising field H , so that if $n < n_T(0)$, we may observe a giant negative magnetoresistance when $n_T(H)$ reaches n .

On the high-density side, the range of inhomogeneous states is restricted by a limiting value n_L , which can be found from the condition

$$\frac{2}{5} \mu_L + \frac{3}{2} \left(\mu_L^2 \frac{e^4}{\epsilon_0} n_L^{1/3} \right)^{1/3} = \frac{AS n_F}{4 n_L} \left(1 - \frac{H}{2|J|} \right), \quad (6.7)$$

$$\mu_L = \frac{(6\pi^2 n_L)^{2/3}}{2m^*} \quad (2\mu_L < AS).$$

If $n > n_L$, a full ferromagnetic order is established.

The field dependence of the moment of the system is as follows: in a weak field, it should rise strongly with the field until moments of all ferromagnetic domains become identically oriented. Then, the rise slows down strongly. In these fields, the increase of the moment with the field is mainly due to the increase in the magnetization of the antiferromagnetic part of the crystal. It is clear from Eq. (6.7) that an inhomogeneous state disappears if the field is sufficiently strong.

The results of numerical calculations carried out for $T_N = 10^\circ \text{K}$, $AS = 0.5 \text{ eV}$, $m^* = 10^{-27} \text{ g}$, $\epsilon_0 = 20$, $a^3 = 2.5 \times 10^{-23} \text{ cm}^3$ are plotted in Fig. 14, where ΔE is the energy gain due to transition to an inhomogeneous state (calculated per one conduction electron), R is the radius of a ferromagnetic sphere, and x is the relative increase in the electron density in the ferromagnetic part of the crystal (in the range $[n_A, n_F]$, the energy is measured from the energy of a canted configuration). It is clear from Fig. 14 that each ferromagnetic sphere contains about 50 electrons.

In nondegenerate antiferromagnetic semiconductors, each electron is localized at its own donor. In this case, an electron can produce a ferromagnetic order in the vicinity of such a donor and the radius of the ordered region is R_d . This state can be regarded as a localized ferron. Each defect has a giant moment $M \sim R_d^3$ but, in the case of substitutional impurities, this moment is linked to a given sublattice. If the field is perpendicular to the antiferromagnetic vector, the moment of a defect is deviated by the field more than the sublattice moment to which it belongs. A detailed calculation [196] shows that the relative contribution of defects to the initial magnetic susceptibility of a crystal is $(R_d/a)^5 \nu_d$. If

$R_d = 2.5a$ and the relative concentration of defects is $\nu_d = 3 \times 10^{-3}$, their contribution is $\sim 30\%$. Even in relatively weak fields, a complete magnetization is achieved and then the susceptibility approaches the value expected for a defect-free crystal.

However, we can have cases in which the moment of a localized ferron is not linked to the moment of a definite sublattice (this applies, for example, to an electron captured by an anion vacancy). Then, the interaction between defects may give rise to a ferromagnetic ordering of their moments.^[48] In anisotropic crystals, this may be due to the dipole-dipole interaction even when the distances between defects are relatively large. In those cases when the orbits of neighboring donors overlap significantly, we find that the electron spins become oriented parallel to one another because this reduces the loss of energy in the establishment of the defect moments. Clearly, this mechanism is not related to any specific crystal symmetry. Thus, when the distance between defects is reduced, the whole crystal may assume a ferromagnetic state, but still remain an insulator because of the weak overlap of the neighboring orbits. A collective state of impurity electrons and a transition to the conducting state occur at still higher carrier densities.

The existence of collective ferron states in degenerate EuTe and EuSe was demonstrated experimentally in^[106, 212]. Measurements of the magnetic susceptibility carried out in^[106] established that iodine-doped EuTe exhibited a spontaneous moment. This moment (per atom) was $1.2 \mu_B$ for the most heavily doped sample, which corresponded to the ratio of the volumes of the ferromagnetic and antiferromagnetic phases $x = 5$. The spontaneous moment disappeared at $T \sim 20^\circ\text{C}$. The existence of the ferromagnetic phase in these samples was confirmed also by a very strong Faraday rotation of the plane of polarization of light, which was independent of the wavelength and due to ferromagnetic resonance. Like the spontaneous moment, this effect disappeared at $\sim 20^\circ\text{K}$ (Fig. 15a).

A large part of an EuTe crystal was antiferromagnetic for $x = 5$ and the ferromagnetic part should be multiply connected. This was confirmed also by the lack of dependence of T_N on n . It could be argued on this basis that practically all electrons were concentrated in the ferromagnetic part of a crystal, which was confirmed by the rapid rise of the conductivity as a result of heating.

The existence of ferron states in degenerate EuTe was demonstrated also in^[38] although the results in that paper were actually interpreted using the canted antiferromagnetic ordering process. Figure 15b shows magnetic-field dependences of heavily doped and pure EuTe crystals at 42°K .^[38] These dependences are of the same type as those reported in^[106]: the initial fast rise of the magnetization of a conducting sample, due to the orientation along the field of the moment of ferromagnetic regions, is followed by further rise of the magnetization at the same rate as for a pure antiferromagnet. This shows that the rise is due to the appearance of magnetization in the antiferromagnetic part of the crystal. As in^[106], the value of T_N is independent of n . According to Fig. 15b, we have $x = 20$, i.e., the ferromagnetic part of the crystal is multiply connected. Consequently, when the temperature is raised, the destruction of inhomogeneous states and conduction elec-

tron delocalization, initially forbidden in ferromagnetic drops, should result in a strong rise of the conductivity. This was indeed observed for the sample in question: at 4.2°K , its resistivity was two orders of magnitude higher than at 77°K but, in the range from 77 to 300°K , it did not vary greatly. The carrier density was $\sim 10^{19} \text{ cm}^{-3}$ at 77°K , which was in order-of-magnitude agreement with the results of calculations for $x = 20$ (Fig. 14). The assumption of a canted antiferromagnetic order failed to explain for the temperature dependence of the conductivity.

Very full information, demonstrating convincingly the existence of ferromagnetic regions in the degenerate metamagnetic semiconductor EuSe, is reported and adequately interpreted in^[212]. The initial magnetic susceptibility of sample No. 1 with $n(300^\circ\text{K}) \sim 6 \times 10^{18} \text{ cm}^{-3}$ exhibited a sharp peak at the Néel point, whereas a different sample with $n(300^\circ\text{K}) = 3.5 \times 10^{19} \text{ cm}^{-3}$ had a very weak peak (Fig. 16a). The field dependence of the moment indicated that sample No. 4 had a spontaneous magnetization representing $\sim 60\%$ of the maximum possible value. The magnetic data taken as a whole demonstrated that the ferromagnetic region of sample No. 1 was multiply connected, whereas, in sample No. 4, it was singly connected.

This was supported by the low resistivity and its weak dependence of the magnetic field in the limit $T \rightarrow 0$ (Fig. 16b). The temperature dependence of the resistivity of sample No. 4, characterized by a maximum in the vicinity of the Curie point ($\sim 20\%$), was typical of heavily doped semiconductors. On the other hand, the resistance

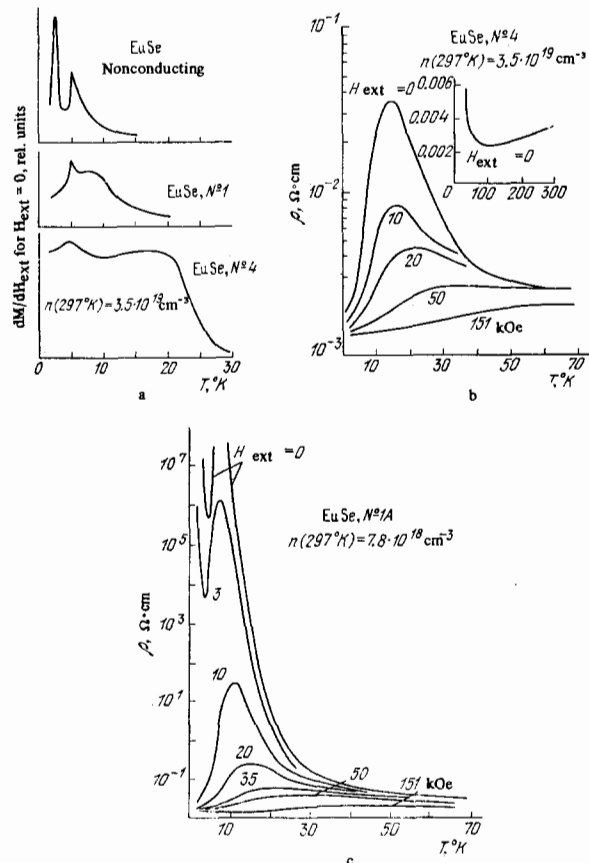


FIG. 16. Magnetic susceptibility of EuSe sample No. 1 with $n(297^\circ\text{K}) \sim 6 \times 10^{18} \text{ cm}^{-3}$ (a), resistivity of EuSe sample No. 4 (b), and resistivity of EuSe sample No. 1A (c).

of sample No. 1A at $T = 1.6^\circ\text{K}$ was very high but it fell by 10 orders of magnitude and approached the resistivity of sample No. 4 even in a field of ~ 10 kOe, which transformed the metamagnet EuSe to a ferromagnetic state (Fig. 16c). When the temperature was raised to 20°K , it also fell strongly but beyond this it depended very weakly on T . This confirmed the prediction that, in the limit $T \rightarrow 0$ and $H \rightarrow 0$, all electrons should be trapped in isolated ferromagnetic drops. It is interesting to note that the carrier densities in these two samples, whose resistivities differed by ten orders of magnitude at 1.6°K , disagreed by a factor of just 5.

c) Screening and Scattering of Electrons in Degenerate Ferromagnetic Semiconductors

The application of an external electric field Φ_q^{ext} to a ferromagnetic semiconductor produces not only an internal electric field Φ_q but also components M_q of a magnetic moment with the same wave vector q . This is due to the fact that a field-induced change in the electron density alters also the indirect exchange intensity. The field Φ_q^{ext} acting on an electron in a crystal is not limited to Φ_q because the appearance of M_q alters the exchange between electrons and the d spins. For this reason, we have to introduce, in addition to the conventional permittivity $\epsilon(q) = \Phi_q^{\text{ext}}/\Phi_q$, describing the action of an external field on a test spinless particle inside a crystal, an additional effective permittivity $\tilde{\epsilon}(q) = \Phi_q^{\text{ext}}/\tilde{\Phi}_q$ which depends on the electron spin. We shall consider the case of total spin polarization of electrons and find $\tilde{\epsilon}(q)$ only for the relevant spin direction.

The special nature of the cooperative phenomena in ferromagnetic semiconductors is due to a positive feedback between the electron density and magnetization: the higher the density in a given region, the higher is the degree of ferromagnetic order in this region at $T \neq 0$ and, consequently, the lower is the position of the bottom of the conduction band. Therefore, there is a tendency for a further rise of n in this region (in the spin-wave approximation we can speak of the attraction between electrons via real magnons^[52]). Consequently, the charge is screened more strongly by electrons than at $T = 0$.

The situation in a ferromagnetic semiconductor can be illustrated by calculating in a clear but not completely consistent manner the permittivities $\epsilon(q)$ and $\tilde{\epsilon}(q)$ in the long-wavelength limit for $W \gg AS$ and $I = 0$. According to Eq. (3.3), the average energy of the interaction between an electron and magnons, obtained for the range $T > T_c/S$ bearing in mind the smallness of the electron momentum, is

$$V = \sum_q C_{0q0} m_q \approx T \sum_q \frac{C_{0q0}}{\omega_q} = \frac{TN}{n} = \frac{T}{\nu} \quad (6.8)$$

because $\omega_q \approx C_{0q0} 0^n$ [Eq. (5.2a)]. In the quasiclassical approximation, we have

$$\mu(r) = \frac{[6\pi^2 n(r)]^{2/3}}{2m^*}, \quad \mu(r) = \mu - e\Phi(r) - T[\nu^{-1}(r) - \nu^{-1}], \quad (6.9)$$

where μ is the electrochemical potential of the system and $\nu = \bar{\nu}(r)$ is the average density. Linearization of Eq. (6.9) gives the relationship between the Fourier component of the density n_q and Φ_q :

$$n_q = -\frac{3}{2} \frac{en}{\mu(1-\Gamma_0)} \Phi_q; \quad \Gamma_0 = \frac{3}{2} \frac{T}{\mu\nu}. \quad (6.10)$$

The application of the Poisson equation

$$n_q = -\frac{q^2}{4\pi\epsilon_0} [e(q) - \epsilon_0] \Phi_q \quad (6.11)$$

and of Eq. (6.9) gives the following expression for $\epsilon(q)$:

$$\frac{\epsilon(q)}{\epsilon_0} = 1 + \frac{\lambda^2}{q^2(1-\Gamma_0)}, \quad \lambda^2 = \frac{6\pi e^2 n}{\mu\epsilon_0}, \quad (6.12)$$

where ϵ_0 is the permittivity of a pure crystal.

Since $\tilde{\Phi}_q = \Phi_q + V_q/e$, we find that the expression for $\tilde{\epsilon}(q)$ obtained using Eqs. (6.8) and (6.10) is

$$\tilde{\epsilon}(q) = \epsilon(q)(1-\Gamma_0). \quad (6.13)$$

In general, calculations of response functions are much more complex operations. They are carried out in^[51, 52] for $W \gg AS$ and in^[182] for $W \ll AS$. In the case of a wide-band heavily doped ferromagnetic semiconductor with $\mu \gg e^2 n^{1/3} \epsilon_0$, we obtain the following expressions for low values of q :

$$\left. \begin{aligned} \epsilon(q) &= \epsilon_0 + \frac{4\pi e^2}{q^2} \Pi_q, \quad \Pi_q = \Pi_q^0 (1-\Gamma_q)^{-1}, \quad \Pi_q^0 \approx \frac{\partial n}{\partial \mu} \left(1 - \frac{q^2}{12k_F^2}\right), \\ \Gamma_q &\approx \Gamma_0 \left(1 - \frac{q^2}{\kappa^2}\right), \quad \Gamma_0 = \frac{3}{8T} \frac{A^2 \nu}{\mu} \frac{1}{N} \sum_q \left(\frac{q^2}{q_0^2 + q^2}\right)^2 m_q (1 + m_q), \\ &\frac{1}{\kappa^2} = \frac{1}{q_0^2} + \frac{1}{12k_F^2}, \\ &\left(q_0^2 = 2m^*AS, \quad k_F^2 = 2m\mu, \quad \nu = \frac{n}{N}\right). \end{aligned} \right\} \quad (6.14)$$

If allowance is made for the field-induced s-d exchange, it is found that a conduction electron with an "up" spin ($A > 0$) experiences an effective field

$$\tilde{\Phi}(q) = \frac{\Phi(q)}{\epsilon(q)}, \quad \tilde{\epsilon}(q) = \epsilon(q)(1-\Gamma_q). \quad (6.15)$$

Applying the expressions in Eq. (6.14), we can readily establish that, if $T < T_e$, where $\Gamma_0(T_e) = [1 \pm (2\lambda/\kappa)]$, the screened potential of a point charge falls in the usual exponential manner. The screening radius decreases with increasing T : $r_e(T) = \lambda^{-1} \sqrt{1 - \Gamma_0(T)}$, where $\lambda^2 = 6\pi n e^2 / \epsilon_0 \mu$. In the interval $[T_-, T_+]$, the screened potential becomes oscillatory:

$$\varphi(r) = \frac{e}{\epsilon_0 r} \exp(-\alpha_+ r) \left[\cos \alpha_- r + \frac{\kappa(1-\Gamma_0)}{\sqrt{2\alpha_+ \alpha_-}} \sin \alpha_- r \right], \quad (6.16)$$

$$\alpha_{\pm} = \frac{1}{2} \sqrt{2\lambda\kappa \pm (1-\Gamma_0)\kappa^2}$$

(subject to the heavy doping conditions $\lambda \ll k_F$ and $\lambda \ll \kappa$).

According to Eq. (6.16), the screening radius passes through a minimum at T_- , rises again when T is increased still further, and becomes infinite at T_+ . The amplitude of the oscillations of the potential also rises with T and becomes infinite at T_+ . The effective potential of Eq. (6.15) acting on electrons behaves in a similar manner. According to Eq. (6.14), the temperature dependence of this potential at $T < T_-$ is the same as that of a pure crystal with a temperature-dependent permittivity $\tilde{\epsilon}_0 = \epsilon_0(1-\Gamma_0)$. In the interval $[T_-, T_+]$, the expression for this potential differs from Eq. (6.16) only by the oscillation amplitude.

The reduction in $r_e(T)$ with rising T is due to an enhancement of the attraction of electrons to one another via magnons. At temperatures $T > T_-$, the screened charge is even overcompensated by the screening electrons so that oscillations of the screened potential are induced. At $T > T_+$, a homogeneous state becomes unstable in the presence of even negligible fluctuations (Sec. d in Chap. 6).

Electrical properties of heavily doped semiconductors are strongly influenced by the random distribution of

impurities. A special feature of ferromagnetic semiconductors is the strong dependence of $\tilde{\epsilon}(q)$ on T which results in a corresponding strong dependence on T of the interaction between electrons and defects. This is frequently responsible for the rise of the resistivity of a ferromagnetic semiconductor with temperature in the range $T < T_c$, although it is usually attributed to the scattering of electrons by magnons. In fact, the relaxation time τ_k of electrons with a momentum k , scattered by ionized impurities, can be obtained for $T < T_c$ from the usual Conwell-Weisskopf formula by replacing ϵ_0 with $\tilde{\epsilon}_0 = \epsilon_0(1 - \Gamma_0)$, where Γ_0 is given by Eq. (6.14):^[222]

$$\frac{1}{\tau_k} = \frac{2\pi e^4 n m^*}{\epsilon_0^2 k^3} \left[\ln(1 + \tilde{\eta}) - \frac{\tilde{\eta}}{1 + \tilde{\eta}} \right], \quad \tilde{\eta} = \frac{4k^2 \tilde{\epsilon}_0}{\lambda^2 \epsilon_0}. \quad (6.17)$$

The above formula is valid for $\eta \gg 1$ and, in this formula, $\ln \eta$ amounts to just a few units and it depends weakly on T . Bearing this in mind, we find that a comparison of Eqs. (6.17) and (3.10) shows that the rise of the resistivity ρ due to the scattering by defects is $e^4 (\epsilon_0^2 a^2 W T)^{-1}$ times greater than the magnon contribution to the resistivity. If $\epsilon_0 = 20$, $a = 5 \text{ \AA}$, and $W = 5 \text{ eV}$, this ratio is 1 at $T = 50^\circ \text{K}$. Consequently, T_c should be several times higher. Thus, the dependence of ρ on T of a ferromagnetic semiconductor with a fairly low T_c should be governed by the scattering on defects. In the range $T_c/S < T < T_c$, the difference $\rho(T) - \rho(0)$ should be, like Γ_0 of Eq. (6.14), proportional to T , whereas, in the magnon scattering mechanism, described by Eq. (3.10), it should be proportional to T^2 .

The physical cause of the increase in the scattering by defects with T is as follows: at $T \neq 0$, the random distribution of impurities gives rise to fluctuations not only in the electrostatic potential and electron density but also (because of the latter) in the local magnetic order, which become stronger with rising temperature. Clearly, fluctuations in the local magnetic order become strongest in the vicinity of T_c and they disappear when T is increased still further. Therefore, the scattering by these fluctuations should pass through a maximum near T_c . Qualitatively, it is clear that the peak of ρ should increase with $\Gamma_0(T_c)$. At sufficiently high values of n , when the indirect exchange via conduction electrons is important, the latter quantity decreases with increasing n and the amplitude of the peak should fall, in agreement with the experimental results (see, for example, Fig. 18). A comparison of the theoretical and experimental results obtained for samples with relatively low values of n is difficult because the condition of heavy doping may not be satisfied.

Another reason why a peak of ρ appears near T_c is the transfer of electrons to zero-current states in the tail extending into the forbidden band. This tail is due to the random distribution of impurities. In the quasi-classical approximation, the density of electron levels in the tail is given by the same expressions as in^[183, 184] but only the mean-square fluctuation potential $\tilde{\Phi}_a \sim \tilde{\epsilon}_0^{-2}$ increases with T as $(1 - \Gamma_0)^{-2}$. Thus, the number of electron states within the forbidden band in the energy

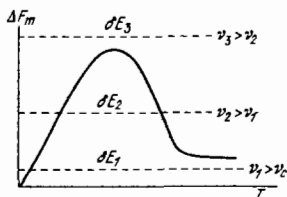


FIG. 17. Energy scheme of the metal-insulator transition in a ferromagnetic semiconductor.

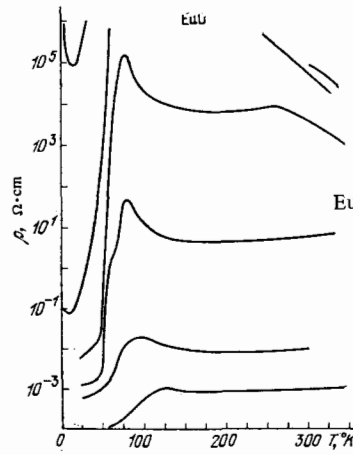


FIG. 18. Resistivity of degenerate EuO and the metal-insulator transition.

range where it is proportional to $\exp[-E^2(e\tilde{\Phi}_a)^{-2}]$ rises exponentially with temperature in the range $T < T_c$.^[51]

The scattering of electrons by magnetic order fluctuations is very sensitive to a magnetic field. This field may reduce or enhance these fluctuations. A reduction is observed when the magnetization in regions with a higher electron density is practically equal to the limiting value and the field can raise the magnetization in regions with lower density. In the opposite limit, when there is no magnetization in $H = 0$, the application of a magnetic field produces a magnetization whose value fluctuates with the electron density.

Moreover, the application of a field increases the degree of spin polarization of electrons if this degree is not yet maximal in $H = 0$. This increases the kinetic energy of electrons which, in accordance with Eq. (6.17), weakens their scattering by defects. If the field reduces fluctuations, these two factors act in the same way and produce a negative magnetoresistance which is exhibited by practically all ferromagnetic semiconductors (see, for example, Figs. 20 and 23). However, if the field enhances fluctuations, the competition between these two factors can make the magnetoresistance positive or negative, depending on T , n , and H .

A simple calculation^[223] demonstrates the possibility of a positive magnetoresistance in a ferromagnetic semiconductor at $T \gg T_c$ and in an antiferromagnetic semiconductor at $T \gg T_N$. If the field is sufficiently strong for all the electrons to be spin-polarized ($AM > \mu$), we find that the energy V of Eq. (6.8) can be expressed in terms of the magnetization M :

$$V(r) = -\frac{AM(r)}{2}, \quad M(r) = \frac{S(S+1)}{3T} \left[H + \frac{1}{2} Av(r) \right] \quad (0 < M < S). \quad (6.18)$$

Using Eqs. (6.8)–(6.18), we obtain a formula for $\epsilon(q)$ which differs from Eq. (6.12) only by the form of Γ_0 :

$$\Gamma_0 = \left(\frac{n}{n_c} \right)^{1/3}, \quad n_c = \frac{2(6\pi^2)^{2/3} WT}{3A^2 S(S+1)}. \quad (6.19)$$

The use of Eqs. (6.17) and (6.19) gives, with logarithmic precision, the following expression for the conductivity (it is assumed that the scattering by impurities predominates):

$$\frac{\sigma(H) - \sigma(0)}{\sigma(0)} = 2 \left[1 - \left(\frac{n}{n_c} \right)^{1/3} \right]^2 - 1. \quad (6.20)$$

If at $T \gg T_c$ there is a temperature range in which $n \geq 0.03n_c$, it follows from Eq. (6.20) that the magnetoresistance in this range is positive. However, when T

risers and n_c of Eq. (6.19) increases proportionally, this inequality is reversed and the magnetoresistance is negative, as at $T < T_c$. This result is in agreement with the experimental data (Sec. e in Chap. 6). A positive magnetoresistance due to the scattering by magnetization fluctuations is possible also in an antiferromagnetic semiconductor at $T = 0$ if it is still in a homogeneous state.^[199]

Shapira and Kautz^[224] explain their observations of a positive magnetoresistance by reduction in the screening radius in a magnetic field, which enhances the scattering by defects. The contribution of magnetic-order fluctuations to the scattering is ignored. This interpretation meets with difficulties: according to Shapira and Kautz,^[224] this effect is obtained from Eq. (6.17) with $\epsilon_0 = \epsilon_0$ only for $\eta < 3$. However, Eq. (6.17) is valid only for $\eta \gg 1$.^[225]

A semiphenomenological calculation of $\epsilon(q)$ of a ferromagnetic semiconductor is made in^[179]. The s-d exchange is taken in the form $AS/2$ and the electron spins are assumed to be directed along the moment of a crystal, which is true if the temperature is not too close to T_c . The free energy of the magnetic subsystem is described by an expansion in terms of the magnetization, which is valid only in the vicinity of T_c . Nevertheless, the qualitative features of $\epsilon(q)$ are predicted correctly in^[179]. The permittivity $\epsilon(q)$ of a ferromagnetic semiconductor is calculated in^[180] subject to the condition $\mu \gg AS$. In this calculation the attention is concentrated on magnetoelastic waves and ferron effects are not investigated.

d) Collective Ferron States and Phase Transitions with Conductivity Jump in Degenerate Ferromagnetic Semiconductors

It follows from the results obtained in Sec. c in the present chapter that, at $T > T_+$, a homogeneous state is absolutely unstable, i.e., the effective attraction between electrons produces regions with an enhanced degree of ferromagnetic order and a higher electron density (a somewhat different condition of absolute instability is obtained in^[210]). The question of the nature of the phase transition to an inhomogeneous state for $\mu \gg e^2 n^{1/3} / \epsilon_0$ can be analyzed using the expression for the free energy F of a system allowing for the slowly varying (in space) small fluctuations of the density n_q . The correction to F , which is due to fluctuations of the momentum q , is given by the expression^[52] [the quadratic term can be obtained in terms of $\epsilon(q)$, as described in^[226]]:

$$\left. \begin{aligned} F_q &= \frac{e_q}{11q} |n_q|^2 + C |n_q|^4 \quad (n_q = n^*_q), \\ C &= \frac{d^4}{dn^4} \left[\frac{3}{5} \mu(n) n + f_m(n) \right], \\ f_m(n) &= T \sum_q \ln \left\{ 1 - \exp \left[-\frac{\omega_q(n)}{T} \right] \right\}, \end{aligned} \right\} \quad (6.21)$$

where f_m is the free energy of magnons found allowing for the indirect exchange [Eq. (5.2a)]. The contribution of thermal excitations of electrons can be ignored in Eq. (6.21) because these excitations are proportional to $(T/\mu)^2$.

It follows from Eq. (6.14) that the ratio ϵ_q / Π_q is smallest when the wave vector is $p = \sqrt{\lambda\kappa}$. This ratio ϵ_p / Π_p vanishes at $T = T_+$. Thus, the divergence of the screened potential at $T = T_+$ means that the free energy decreases with rising amplitude of the fluctuations at

$T > T_+$. Within the framework of the approach adopted here, it is meaningful to consider only the temperatures T_+ below T_c . If T is much higher than T_c , the transition to an inhomogeneous state is impossible for the same reasons which forbid individual ferrons. Since $T_+ \approx (d\Gamma_0/dT)^{-1}$, it follows from Eq. (6.14) that a homogeneous state is stable not only at very low but also at very high values of n . This can be explained by the very high Fermi energy so that the loss of this energy due to a transition to an inhomogeneous state cannot be compensated by the gain in the s-d exchange energy.

The nature of the phase transition can sometimes be deduced from the sign of the coefficient $C(T_+)$ in Eq. (6.21). This coefficient is negative for $\nu < 10IS/W$. Then the transition is necessarily of first order and it should occur at some temperature T_1 below T_+ . In fact, at $T = T_+ + \delta$ (where $\delta \rightarrow 0$), a homogeneous state does not correspond even to a relative minimum of F . Consequently, the absolute minimum of F should be reached for sufficiently large fluctuations. At $T = T_+ - \delta$, a homogeneous state corresponds to a very shallow minimum of F but clearly this minimum lies much higher than the principal minimum whose position is practically unaffected by small temperature variations. On the other hand, at $T = 0$ a homogeneous state corresponds to the absolute minimum of F and, therefore, sufficiently far from T_+ the minima corresponding to homogeneous and inhomogeneous states lie at the same level. For $C > 0$, a phase transition occurring at T_+ should be of second order. However, such a transition need not occur discontinuously at $T_1 < T_+$.

A phase transition of first order produces a state analogous to that discussed in Sec. b in the present chapter, i.e., a crystal splits into alternate regions with high and low values of the electron density and momentum. At $T < T_1$, an inhomogeneous state may be metastable and the resistivity in this state can, for obvious reasons, be higher than the resistivity in a stable homogeneous state. An estimate of T_+ obtained from Eq. (6.14) for $\epsilon_0 = 20$, $AS = 0.5$ eV, $m^* = 10^{-27}$ g, $T_c = 20^\circ\text{K}$, $n = 10^{20}$ cm⁻³, and $N = 10^{22}$ cm⁻³ gives $T_+ \approx 10^\circ\text{K}$ and $C < 0$. This is in qualitative agreement with the experimental data on EuS (Fig. 22)^[82]—see Sec. e in Chap. 6.

It is quite difficult to calculate the structure of an inhomogeneous state of a ferromagnetic semiconductor. Such a calculation is reported in^[227], where it is shown that the formation of low-conductivity drops inside a highly conducting matrix may be thermodynamically favorable. Therefore, the transition to an inhomogeneous state need not be accompanied by a large change in the conductivity. An inhomogeneous state of a pure ferromagnetic semiconductor in which carriers are generated optically is investigated in^[228]. Regions of radius of the order of the diffusion length with a high degree of ferromagnetic order and high electron and hole densities may appear in such a crystal.

In a certain range of impurity concentrations, a transition from a conducting to an insulating state may take place in a ferromagnetic semiconductor.^[90, 196] At $T = 0$, the behavior of a doped ferromagnetic semiconductor depends on n in the same way as that of nonmagnetic semiconductors: there is a critical donor density n_c below which the crystal is an insulator and above which it is a semimetal. The phase transition to a collective ferron state occurs at a value of n slightly higher than n_c because the potential of an impurity atom at $T = 0$ is

"almost sufficient" for the capture of an electron. It becomes sufficient at finite values of T since then the electrostatic potential is supplemented by the potential of the exchange forces resulting from the presence of an excess magnetization at a donor. This distinguishes the transition at $n \sim n_c$ from the transition which occurs at $n \gg n_c$ when electrons are not captured by localized states because fluctuations of the impurity potential are too small ($\mu \gg e^2 n^{1/3} / \epsilon_0$). As in the $n \gg n_c$ case, we can show that the phase transition is of first order. This is confirmed by the experimental results obtained for EuO (Fig. 18): the conductivity jump at the transition is sharp but there is some smearing due to the random distribution of impurities. Therefore, the transition is investigated by comparing the free energies F_i and F_c in the insulating and conducting states. As pointed out earlier, the temperature-dependent part of F consists of just the free energy of magnons F_m . The electron density is distributed inhomogeneously in space because of the fluctuations of the impurity potential. If the Bohr radius of an electron at a donor is sufficiently large, the electron density varies slowly in space even in the insulating state. This applies even more strongly to the conducting state. Therefore, in the temperature range $T_c/S < T < T_c$, we can apply the quasiclassical approximation to magnons, i.e., we can assume that ω_q depends on r and the free energy of magnons E_m , subject to Eq. (6.21), can be represented in the form

$$F_m = \int f_m [n(r)] d^3r \approx \frac{TV}{(2\pi)^3} \left[\int d^3k \ln \left(\frac{\bar{\omega}_k}{T} \right) - \frac{A^2 v^2}{8} D^2 G \right],$$

$$D^2 = \frac{1}{V} \int d^3r \left[\frac{v(r) - v}{v} \right]^2, \quad G = \int \frac{d^3q}{\omega_q^2} \left(\frac{q^2}{q_0^2 + q^2} \right)^2, \quad (6.22)$$

where $\bar{\omega}_k$ is the frequency corresponding to the average electron density ν . The system (6.22) is derived on the assumption that the spatial dispersion of the magnon frequencies is slight.

Since the dispersion of the density D^2 in the insulating state is higher than in the conducting state, whereas all the other terms in Eq. (6.22) are the same for both states, it follows that the free energy of the insulating state decreases more rapidly with rising T than the free energy of the conducting state (Fig. 17). This is due to the fact that, in the insulating state, the magnetic order in the regions with a higher electron density is destroyed more slowly than in the conducting state. The difference ΔF between the free energies of spins in the conducting and insulating states passes through a maximum in the region of T_c , where the magnetic order is completely destroyed in the conducting state but is still retained in the vicinity of donors in the insulating state. A further rise of T begins to destroy the magnetic order also in the insulating state and, therefore, ΔF decreases. However, even in the limit $T \rightarrow \infty$, the difference $\Delta F(\infty)$ remains finite for the same reason that the depth of local levels remains larger than at $T = 0$ (see Sec. d in Chap. 3). These conclusions remain in force if the Bohr orbit radius is small.^[90]

If the electron states in the conducting and insulating phases are very different, then ΔF depends weakly on ν for $\nu - \nu_c \ll \nu_c$. Unfortunately, little is known at present about the difference δE between the energies of insulating and conducting states. Clearly, this difference should increase with $\nu - \nu_c$. Therefore, depending on the value of this difference, we can have three types of situation (Fig. 17): 1) in the range of very low values of the difference $\nu - \nu_c$, the straight line representing δE intersects the curve ΔF (i.e., the free energies of the conducting

and insulating states become equal) at just one point T_{M_2} ; this means that, after transition to the insulating state, a crystal remains in that state right up to the highest temperatures; 2) in the range of larger values of $\nu - \nu_c$, there are two points of intersection, T_{M_1} and T_{M_2} , i.e., the transition to the insulating state is followed by the reverse transition to the conducting state, which is manifested as a sharp resistivity peak between T_{M_1} and T_{M_2} ; 3) at still higher values of ν , there are no intersections, i.e., the transition to the insulating state does not occur at all. The shallower the local level, the smaller is the difference $\Delta F(\infty)$ and the more difficult it is to observe the metal-insulator transition. If a donor can capture two electrons (this applies to, for example, an oxygen vacancy in EuO), the total spin of these electrons may be zero in the insulating state. The phase transition to this state is still possible but it is no longer due to the ferron effect but due to a strong reduction in the influence of the electrons on the magnetic order when spins are paired and due to a corresponding reduction in the magnon frequencies [$\omega_q(r)$ approaches ω_q^0]. However, according to Eqs. (6.21) and (6.22), the free energy of magnons decreases with increasing "softness" of their frequencies.

An attempt to develop a theory of the metal-insulator transition in EuO as a cooperative phenomenon is made in^[179] by generalization of the theory of collectivization of the Mott-donor electrons^[231] to a medium with a temperature-dependent permittivity $\epsilon(q)$. The physics of the phenomenon considered in^[179] is essentially the same as that described above but the calculations are based on an idealized model.

The metal-insulator transition in EuO:Eu is explained in^[109] assuming that, at high temperatures, electrons are in local levels whose depth depends weakly on T . At the same time, the bottom of the conduction band drops with decreasing T and, when it falls below these local levels, the crystal becomes conducting. It is suggested in^[229] that these levels are due to oxygen vacancies, each of which can capture two electrons with antiparallel spins, whereas, in^[188], it is postulated that the spins are parallel and the weak dependence of the level positions on T is attributed to a high degree of magnetic order in the vicinity of a vacancy that has captured electrons ("localized ferron"). According to the picture developed in^[109, 229, 188], the delocalization of each electron occurs independently of the other electrons, i.e., the effect should be independent of n .

This approach fails to explain why a positively charged defect (oxygen vacancy) cannot capture an electron at $T = 0$. It follows from the theory of heavily doped semiconductors^[231] that the delocalization of the donor electrons is possible only if the donor concentration is sufficiently high and it is essentially a cooperative phenomenon. Therefore, the metal-insulator transition in a heavily doped ferromagnetic semiconductor should be cooperative, i.e., it should be a phase transition which depends strongly on n . This is confirmed by the experimental results (Sec. e below); it occurs only in a very narrow range of electron densities.

e) Experimental Results on Resistance of Heavily Doped Ferromagnetic Semiconductors

Typical curves showing the resistivity of EuO are plotted in Fig. 18 on the basis of^[109]. Similar results

were reported later in [121, 108, 185-188]. The most remarkable feature of these results is the metal-insulator transition at 50°K exhibited by samples with oxygen vacancies, whose resistivity changes by 13 orders of magnitude. This transition differs greatly from the metal-insulator transitions in V_xO_y -type crystals because of the giant jump (in the latter case, it does not exceed eight orders of magnitude) and because of the inversion of the conducting and insulating phases relative to the transition point. In the insulating phase, the resistivity falls exponentially with T and the activation energy ΔE at $T \gg T_c$ is 0.3 eV. The transition point is shifted by external magnetic fields toward higher values of T and the plot of $\rho(T)$ becomes less steep (Fig. 19). However, even in fields of 140 kOe, the resistivity rises by six orders of magnitude between 70 and 120°K. [121] The information on the nature of the dependences of ΔE on T and H published so far [108, 185, 189] is contradictory.

It is clear from Fig. 18 that the metal-insulator transition does not occur in samples with a high low-temperature conductivity. According to [121], it is observed in the range $n \sim (1-2) \times 10^{19} \text{ cm}^{-3}$ but disappears already for $n \sim 3 \times 10^{19} \text{ cm}^{-3}$. The sensitivity of the transition to the electron density confirms its cooperative nature (Sec. d in Chap. 6). The Curie point of the samples exhibiting the transition is practically undisplaced, compared with pure crystals. However, it is strongly displaced for samples with high values of n .

If the transition does not occur, a typical resistivity peak is observed slightly above T_c of a ferromagnetic semiconductor and this peak has a definite structure; the relative amplitude of the peak decreases with rising electron density. The giant magnetoresistance of EuO near T_c is demonstrated in Fig. 20. [121] According to [121], the metal-insulator transition is practically entirely due to the change in the carrier density, whereas the resistivity peak at high values of n is due to the simultaneous occurrence of a density minimum and a carrier scattering maximum. The former is suppressed

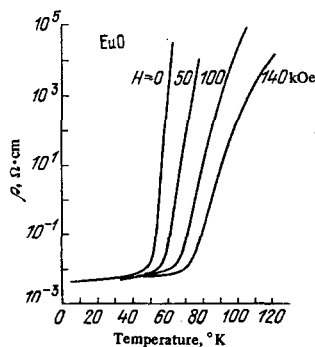


FIG. 19. Metal-insulator transition in EuO in a magnetic field.

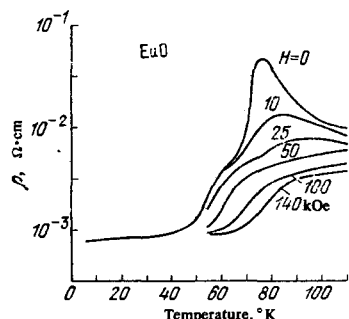


FIG. 20. Magnetoresistance of degenerate EuO.

by fields of a few kilo-oersted, whereas the latter can be destroyed only by very high fields.

The question whether the metal-insulator transition is possible in Gd-doped EuO, for which $\Delta F(\infty)$ is very small, cannot be resolved on the basis of the experimental data [112, 230] because they are contradictory. Crystals of p-type EuO grown in an oxygen atmosphere do not exhibit even a resistivity peak near T_c . [108] Several attempts were made [103, 109, 112] to find the relaxation time τ and the effective mass of carriers in EuO by combining the results of electrical and optical measurements. However, the values obtained, $\tau \sim 10^{-14} - 10^{-15}$ sec, were far too small so that the condition $\tau^{-1} \ll \mu$ of validity of the transport equation used in the calculations [103, 109, 112] was not satisfied.

In contrast to EuO, crystals of EuS with excess Eu do not exhibit a transition to the insulating state but a sharp resistivity peak is observed in the region of T_c . According to [190, 191], these crystals have an additional resistivity singularity of the type that may be expected in the transition of a ferromagnetic semiconductor to an inhomogeneous state (Sec. d in Chap. 6). It is shown in Fig. 21 that, when temperature rises near 8°K, the resistivity increases steeply by about an order of magnitude but cooling does not reduce the resistivity (dashed line in Fig. 21). The high-resistivity state is metastable and it disappears after several minutes; the rate of its decay decreases with time. The metastable state is destroyed also by a magnetic field of a few kilo-oersted and the fall of the resistivity is accompanied by a decrease of the Hall coefficient, which is proportional to $1/n$ (Fig. 22). The effect is mainly due to a change in the carrier density but its value has not yet been determined. Further studies are needed in order to find whether this effect is indeed due to a transition to an inhomogeneous state (Sec. d in Chap. 6).

On approach to T_c , both EuS and EuO exhibit a sharp resistivity peak, which can be destroyed by a magnetic field (Fig. 23). The quantitative results obtained in Sec. c, where the peak is attributed to the interaction of electrons with magnetic moments formed at $T \neq 0$ around defects, apply only to very heavily doped semiconductors. They cannot be used in those cases when the resistivity rises by 5-6 orders of magnitude near T_c and then one has to use the qualitative analysis given in Sec. d in the present chapter.

The interaction of electrons with such magnetic moments is clearly responsible also for the positive mag-

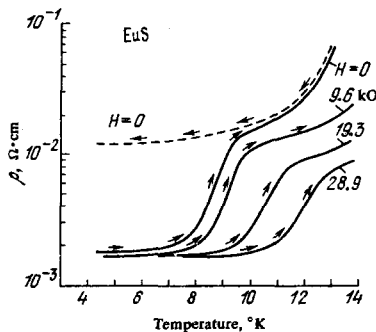


FIG. 21

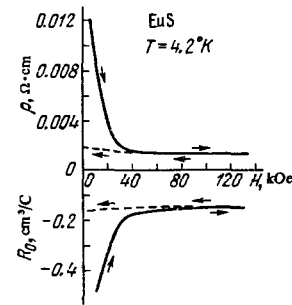


FIG. 22

FIG. 21. Thermal hysteresis of the resistivity of degenerate EuS.

FIG. 22. Hysteresis of the resistivity and Hall coefficient of EuS in magnetic fields.

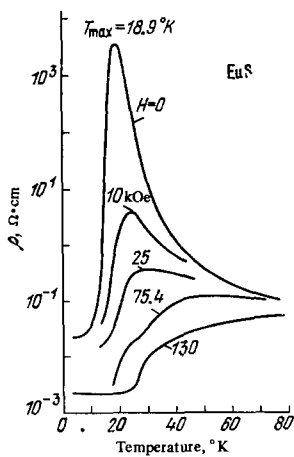


FIG. 23

FIG. 23. Magnetoresistance of degenerate EuS at $T \lesssim T_C$.

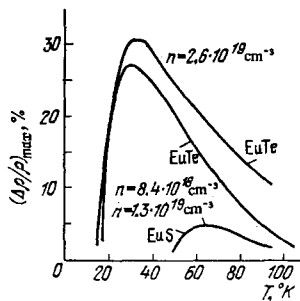


FIG. 24

FIG. 24. Positive magnetoresistance of degenerate EuS and EuTe at $T \gg T_C$.

netoresistance exhibited by heavily doped ferromagnetic semiconductors (EuS^[83]) and antiferromagnetic semiconductors (EuTe^[83] and EuSe^[212]) in a certain range of temperatures in the paramagnetic region (Fig. 24). Outside this range, the magnetoresistance is negative, which is in agreement with the theory given in Sec. c. The field dependence of the magnetoresistance passes through a maximum, whose position shifts with T in the direction of higher fields. The effect reported in^[83, 212] is 3–4 orders of magnitude greater than the corresponding effect in nonmagnetic semiconductors and is independent of the field orientation.

At 300°K, single crystals of EuO:Gd exhibit, like amorphous semiconductors, switching effects which are not observed in pure EuO crystals.^[192] According to^[193], a ferromagnetic semiconductor exhibiting the metal-insulator transition should have an N-type current-voltage characteristic near the transition point and this characteristic is due to thermal effects.

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