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COMBINED RESONANCE IN SEMICONDUCTORS

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1. INFLUENCE OF SPIN-ORBIT INTERACTION ON RESONANCE EFFECTS

IF we neglect spin-orbit interaction, then an electron moves independently in its configurational degrees of freedom, on the one hand, and in the spin degrees of freedom, on the other. Let us consider these motions in succession.

For a band electron (hole) with isotropic quadratic dispersion law, situated in a constant homogeneous magnetic field **H**, the classical picture of configurational motion is rotation along a helix with an axis parallel to **H**, with a revolution frequency

$$\omega_c = \frac{eH}{mc}, \tag{1.1}$$

where *m*—effective mass. In the quantum description, the well-known Landau quantization picture arises, with the neighboring orbits spaced $\hbar\omega_c$ apart.

When an external high-frequency field is superimposed, the electron is acted upon by a Lorentz force which leads to transitions between the stationary states. In the electric-dipole approximation, which in practice is absolutely sufficient, the interaction of the carrier with the electromagnetic field is purely electric; it excites quantum transitions between the neighboring Landau levels ($\Delta n = 1$), corresponding to the usual cyclotron resonance at a frequency ω_c . The characteristic quantity, with dimension of length, determining the dipole moment of the transition, and consequently the intensity of the cyclotron absorption, is $r_H = (c\hbar/eH)^{1/2}$ —radius of the first quantum orbit. In the range of magnetic fields employed in practice, $r_H \sim 10^{-5} - 10^{-6}$ cm.

If the carrier dispersion obeys a complicated law, the cyclotron resonance picture becomes much more complicated. The cyclotron frequency ω_c becomes a function of the magnitude and orientation of the magnetic field **H** and of the number of the cyclotron orbit; transitions with $\Delta n > 1$ become possible. However, the main attributes of cyclotron resonance—the electric character of the excitation and the invari-

ance of the spin state—remain in force.

The two spin orientations of the electron (hole) in the field **H** correspond to two spin levels. Transitions between them—paramagnetic resonance—are excited by the magnetic component of the high-frequency field and occur at a frequency

$$\omega_s^0 = \frac{g_0\beta_0 H}{\hbar};$$

here β_0 is the Bohr magneton and $g_0 \approx 2$ is the *g*-factor of the free electron. The characteristic length defining the intensity of the paramagnetic resonance is the Compton length $\lambda_0 = \hbar/m_0c = 2\beta_0/e \approx 4 \times 10^{-11}$ cm (m_0 —mass of free electron).

It is obvious that $r_H \gg \lambda_0$, and it is seen from the foregoing estimates that these quantities differ by approximately five orders of magnitude. Consequently, cyclotron resonance is stronger than paramagnetic resonance by approximately ten orders. However, this simple and lucid picture is greatly complicated when spin-orbit interaction is taken into account. First, the interaction leads to a change in the numerical values of the band-structure parameters, primarily the spectroscopic splitting factor. Under these conditions, the band carrier is a quasiparticle, which has an effective spin magnetic moment containing besides the pure spin an orbital part, which frequently is dominating; we shall henceforth take the carrier spin to have this generalized meaning. The difference between the *g*-factor and g_0 is largest in crystals consisting of medium and heavy elements.* For example, in InSb the *g*-factor of the band electrons is 25 times larger than the value for free electrons and has an opposite sign. In addition, the *g*-factor changes usually from a scalar into a tensor, the symmetry of which is determined by the

*In such cases, strictly speaking, the characteristic parameter should be taken to be not λ_0 , but $\lambda = |g| \lambda_0/2$. For the sake of simplicity, however, recognizing that such a change can always be made and is significant only in individual cases, we shall not introduce the new parameter λ in what follows.

group properties.

In spite of the great importance of this renormalization of parameters, the most radical change is experienced nevertheless by the quasiparticle dynamics. Namely, the autonomy of the configurational and spin motions is lost and a "coupling" is produced between them. We must emphasize from the very outset that the strong atom-core electrostatic field in which the band electron moves in a crystal causes the spin-orbit effects to be larger by many orders of magnitude for the band electrons than for the free electrons.

The coupling between the configurational and spin motions makes it impossible to separate the quantum transitions into purely configurational and purely spin ones; we can speak only of predominantly configurational and predominantly spin transitions. But this changes appreciably the conditions for the excitation of the different transitions. Namely, it becomes possible to excite spin transitions by the electric component of the electro-magnetic field, and the orbital transitions by the magnetic component; this effect will henceforth be called combined resonance.

The electron interacts with the electric component of the high-frequency field much more strongly than with the magnetic component; a manifestation of this fact is the already-mentioned disparity between the intensities of the cyclotron and paramagnetic resonances. Therefore only the first of these two possibilities is of importance in semiconductors, though it can cause the electric excitation of the spin transitions to prevail over the magnetic excitations even in the case of a relatively weak spin-orbit coupling.

Combined resonance was investigated by us for the first time^[1,2] for band carriers, as applied to a special type of band structure particularly favorable for the production of high combined-resonance intensities, and serving as a convenient model for a theoretical analysis; by now many other cases have been considered and the first experimental confirmations of the existence of this resonance obtained.

In the next two sections we present an exposition of the theory of combined resonance of band carriers in crystals of various types, and an analysis of the first experimental data. It will be shown that in many cases, particularly in crystals without inversion centers, the combined resonance intensity should prevail (sometimes by many orders of magnitude) over the paramagnetic-resonance intensity.

The wave functions of the local centers of large radius can be represented as relatively narrow wave packets, made up of the wave functions of the band states, which are energetically close to the edge of the band. It is therefore natural to expect that the high intensity of the combined resonance with the band carriers should make it possible for an analogous effect to exist for bound carriers. A more detailed analysis shows that combined resonance of

bound electrons can actually occur, but under ordinary conditions it should be much weaker than for the band carriers. The reason for it is that the radius of the center is much smaller than the radius of the orbit. Nonetheless, in certain cases, the combined and paramagnetic resonances may be comparable in intensity, and the former may even be much larger for local centers. A discussion of these questions is contained in the two last sections of the article.

2. COMBINED RESONANCE WITH BAND CARRIERS (GENERAL ANALYSIS)

The motion of a band electron in a constant homogeneous magnetic field \mathbf{H} with vector potential $\mathbf{A}(\mathbf{r})$ is described by a matrix Hamiltonian^[3] which depends on the quasimomentum operator

$$\hat{\mathbf{k}} = -i\nabla + \frac{e\mathbf{A}(\mathbf{r})}{ch}. \quad (2.1)$$

The order of the matrix is equal to the number of contacting (or neighboring) bands at the symmetry point \mathbf{k}_0 , in the vicinity of which the Hamiltonian of the effective-mass method is constructed. We confine ourselves here to the case when account of the spin leads to twofold degeneracy at the symmetry points; it is precisely under such conditions that the phenomenon becomes clearest and the physical picture is the most lucid. This analysis covers at the same time the majority of the most interesting cases which can be investigated experimentally.

It is convenient to transform the matrix Hamiltonian $\mathbf{H}(\hat{\mathbf{k}})$ in such a way, that it contains only symmetrized products of the quasimomentum components. All the resultant commutators should then be expressed in terms of the components of the magnetic field intensity \mathbf{H} with the aid of the well-known commutation relations

$$[\hat{k}_\alpha, \hat{k}_{\alpha'}] = -i \frac{eH_{\alpha\alpha'}}{ch}. \quad (2.2)$$

The triplet of indices α , α' , and α'' constitutes cyclic permutation of x , y , and z . The matrix Hamiltonian

$$\mathbf{H}(\hat{\mathbf{k}}) = \|\mathbf{H}_{ij}(\hat{\mathbf{k}})\| \quad (2.3)$$

is transformed here into a series in powers of \mathbf{H}

$$\mathbf{H}(\hat{\mathbf{k}}) = \sum_{i=0}^{\infty} \mathbf{H}^{(i)}(\hat{\mathbf{k}}, H), \quad (2.4)$$

where the term $\mathbf{H}^{(i)}$ is of the order of H^i .

Inasmuch as the quantum radius in \mathbf{k} -space is $k_H = r_H^{-1} \sim H^{1/2}$, the expansion of (2.4) in powers of \mathbf{H} is effectively also an expansion in powers of \mathbf{k} , and in the spirit of the effective-mass method it is customarily sufficient to retain only the first few terms. We retain in what follows the first two terms. If we adhere to the formal procedure of taking into account terms of one order in the powers of the quasimomentum, we must, for example when retaining in $\mathbf{H}^{(1)}$

terms up to Hk^2 inclusive, confine ourselves in $H^{(0)}$ to terms of order k^4 . However, in those cases when the actual values of k (k_{char} = radius of the Fermi surface, mean thermal k) greatly exceed k_H , it is advantageous to distinguish between the orders of the parameters k_{char} and k_H . We note also that in the case of a narrow forbidden band, when strong non-parabolicity obtains, it may be advantageous to transform the series (2.4) in such a manner as to collect terms with identical symmetry from among the different order in H .

The individual terms $H^{(i)}$ of the Hamiltonian H are best expanded in terms of basis matrices, and in the case of two-dimensional matrices considered here we can take the basis matrices to be the unit matrix σ_0 and the Pauli matrix $\sigma = (\sigma_x, \sigma_y, \sigma_z) = (\sigma_1, \sigma_2, \sigma_3)$; we shall assume these matrices to be chosen in the usual representation ($\sigma_y = \sigma_2$ -imaginary matrix). Then

$$H^{(0)}(\hat{\mathbf{k}}, \mathbf{H}) = \sigma_0(\mathbf{H}\mathbf{B}(\hat{\mathbf{k}}) + \frac{\beta_0}{2}(\sigma\mathbf{g}(\hat{\mathbf{k}})\mathbf{H})), \quad (2.5)$$

where $\mathbf{B}(\hat{\mathbf{k}})$ is a pseudovector and $\mathbf{g}(\hat{\mathbf{k}})$ a tensor.

The spatial symmetry of the crystal and the symmetry with respect to time reversal impose several limitations on the function $f_i(\hat{\mathbf{k}})$, $\mathbf{B}(\hat{\mathbf{k}})$, and $\mathbf{g}(\hat{\mathbf{k}})$. These limitations can be obtained for each concrete type of crystal symmetry, for example, by a method developed by Pikus^[4]. We, however, will be interested only in limitations that are general for all crystals with inversion center.

If we denote by ψ_i ($i = 1, 2$) the Bloch spinors corresponding to the considered twofold degenerate state with quasimomentum \mathbf{k}_0 , then, by successive application of the operations of inversion J and time reversal K , these spinors will be transformed in terms of one another

$$KJ\psi_i = R\psi_i = \sum_j R_{ji}\psi_j, \quad (2.6)$$

where R -unit matrix. This relation will hold both for one-dimensional small representations, when twofold degeneracy is the consequence of T -symmetry,* and for two-dimensional small representations, when the T -symmetry does not lead to additional degeneracy.† Applying to both sides of (2.6) the operator KJ and recognizing that $K^2 = -1$ and $J^2 = 1$, we get $RR^* = -1$, which in conjunction with unitarity of R gives $R = -\tilde{R}$, where \tilde{R} is the transpose of R . We can therefore assume $R = \sigma_y$.

The condition of symmetry with respect to the transformation KJ , for the matrix Hamiltonian written in the basis ψ_i , is of the form

$$H(\hat{\mathbf{k}}, \mathbf{H}) = R^{-1}\tilde{H}(KJ\hat{\mathbf{k}}, KJ\mathbf{H})R = \sigma_y\tilde{H}(\hat{\mathbf{k}}, -\mathbf{H})\sigma_y. \quad (2.7)$$

If we return to the expansion of H in the matrix basis σ_0 and σ , then it follows from (2.7) that σ_0 can be regarded as a real scalar ($KJ\sigma_0 = \sigma_0$), σ as an imaginary pseudovector ($KJ\sigma = -\sigma$), $\hat{\mathbf{k}}$ as an imaginary vector ($KJ\hat{\mathbf{k}} = \hat{\mathbf{k}}$), and \mathbf{H} as an imaginary pseudovector ($KJ\mathbf{H} = -\mathbf{H}$).

Applying the invariance condition (2.7) to (2.5), we obtain

$$f_i(\hat{\mathbf{k}}) = 0 \text{ for } i = 1, 2, 3, \quad \mathbf{B}(\hat{\mathbf{k}}) = 0; \quad (2.8)$$

No limitations whatever are imposed on $f_0(\hat{\mathbf{k}})$ and $\mathbf{g}(\hat{\mathbf{k}})$. If \mathbf{k}_0 is equivalent to $-\mathbf{k}_0$ (in particular, if $\mathbf{k}_0 = 0$), then $H(\hat{\mathbf{k}}, \mathbf{H})$ should be invariant against the inversion J , and in this case f_0 and \mathbf{g} will be even functions of $\hat{\mathbf{k}}$.

The first condition in (2.8) denotes that the matrix $H^{(0)}$ is a multiple of the unit matrix; this leads immediately to the well-known fact that in crystals with inversion center the bands are doubly degenerate in all of \mathbf{k} -space. The second condition of (2.8) shows that in the presence of an inversion center the Hamiltonian term describing the different displacement in the magnetic field of two conjugate valleys vanishes; since we are interested in what follows only in the intravalley transitions, this term will be left out completely.

We now return to the Hamiltonian (2.5) and analyze in greater detail the roles of the individual components.

The term $H^{(0)}$ does not depend explicitly on \mathbf{H} and is determined by the same parameters which enter in the dispersion law and govern the form of the equal-energy surfaces. Consequently it is natural to regard the motion which is determined predominantly by this part of the Hamiltonian as being a generalized configurational motion.

The off-diagonal elements of the matrix $H^{(0)}$ are as a rule much smaller than the diagonal elements, since they describe the divergence of the bands near the point \mathbf{k}_0 due to the spin-orbit interaction. This divergence of the bands, which always takes place in crystals without inversion center, does not occur in the presence of an inversion center.

In a constant homogeneous magnetic field the term $H^{(1)}$ in (2.5), in the lower approximation in which the dependence of $\mathbf{g}(\hat{\mathbf{k}})$ on $\hat{\mathbf{k}}$ can be neglected, is a constant matrix analogous to the spin Hamiltonian. Therefore the motion determined by this term can be naturally regarded as generalized spin motion.

The configuration and spin motions can be regarded as independent when the Hamiltonian consists of two terms (which, of course, commute), one of which depends only on the "configuration" operators ($\hat{\mathbf{k}}$ components), and the second only on the spin operators (σ components). This is precisely the case that occurs when the matrix $H^{(0)}$ is regarded

*Cases a and b according to Wigner^[5]; note that we are considering a quasiparticle with spin 1/2.

†Case c according to Wigner^[5].

as diagonal and the g -factor does not depend on $\hat{\mathbf{k}}$.

Any deviation from this condition leads to non-autonomy of the configurational and spin motion in a homogeneous magnetic field; it is clear from the foregoing that the type of coupling between them is different, depending on whether the crystal has an inversion center.

In crystals with inversion center $H^{(0)}$ is always diagonal, and therefore the only cause of the coupling is the dependence $g(\hat{\mathbf{k}})$.

To the contrary, in crystals without an inversion center, we have besides this effect also coupling due to the off-diagonal nature of $H^{(0)}$. As a rule, it is precisely the latter effect which predominates, since it is connected with terms that can be of the same order as k_{char} (in crystals of the corresponding symmetry groups), whereas the dependence of the g -factor on $\hat{\mathbf{k}}$ is connected with the terms $\sim k^2 \hbar k_{\text{char}}$ or of even higher order of smallness (for k_0 equivalent to $-k_0$, starting with terms $\sim k^2 \hbar k_{\text{char}}^2$).

The matrix Hamiltonian in the presence of an alternating electromagnetic field with vector potential $\tilde{\mathbf{A}}$ in the electric-dipole approximation is obtained from the Hamiltonian written out above by making the substitutions

$$\mathbf{A} \rightarrow \mathbf{A} + \tilde{\mathbf{A}}, \quad \mathbf{H} \rightarrow \mathbf{H} + \tilde{\mathbf{H}}. \quad (2.9)$$

In the approximation linear in $\tilde{\mathbf{A}}$, two terms are added to $H(\hat{\mathbf{k}})$:

$$\tilde{H}_1 = \frac{e}{c} (\mathbf{v} \tilde{\mathbf{A}}), \quad v = \frac{1}{i\hbar} [\mathbf{r}, H(\hat{\mathbf{k}})], \quad (2.10)$$

$$\tilde{H}_2 = \frac{\beta_0}{2} (\boldsymbol{\sigma} g(\hat{\mathbf{k}}) \tilde{\mathbf{H}}). \quad (2.11)$$

In a standing wave, where the electric and magnetic high-frequency fields have different spatial distributions, their effects can be separated. Inasmuch as the former is proportional to $\tilde{\mathbf{A}}$, the perturbation \tilde{H}_1 in the electric-dipole approximation reduces to the action of the electric component of the field (in the general case one should speak of the effect of the Lorentz force), whereas \tilde{H}_2 describes the action of the magnetic component of the field on the effective spin moment.

In the approximation in which the configurational and spin motions can be separated, \tilde{H}_1 is the cause of cyclotron resonance and \tilde{H}_2 of paramagnetic resonance. Because of the coupling between the configurational and spin motions, the operator \tilde{H}_1 begins to excite transitions which are accompanied by a change in the spin state; among these will be both a transition connected with only the change in the spin quantum number, and transitions accompanied by simultaneous change in the spin and configuration quantum numbers. In accordance with the statements made in the preceding section, all these transitions will be classified as belonging to combined resonance, and we shall neglect the combined resonance induced by \tilde{H}_2 .

By way of a measure of the intensity of the spin transitions, it is convenient to choose the paramagnetic-resonance intensity; we shall consequently compare the intensity of the combined resonance with that of the paramagnetic resonance. As will be shown later on, the combined-resonance intensity is in many cases of the same order as the paramagnetic-resonance intensity or appreciably higher, and under certain conditions it may even approach the intensity of the cyclotron resonance.

Notice should be taken of the following circumstance. In the usual relativistic formula for the energy of the spin-orbit interaction of the electron

$$V_{SO} = \frac{e\hbar^2}{4m_0^2 c^2} (\boldsymbol{\sigma} [\mathbf{E}, \hat{\mathbf{k}}]) \quad (2.12)^*$$

the alternating electric field $\tilde{\mathbf{E}}$ is contained twice, once explicitly as part of the total field \mathbf{E} , and also implicitly in terms of the vector potential, which is contained in $\hat{\mathbf{k}}$. The scheme of the matrix Hamiltonian in the form described above corresponds to an account of $\tilde{\mathbf{E}}$ only via the vector potential. We must therefore verify that the explicit dependence of V_{SO} on $\tilde{\mathbf{E}}$ is negligible. Indeed, it is connected with a term of the order of $\beta_0 (\hbar k/m_0 c) \tilde{\mathbf{E}} \sim \beta_0 (v/c) \tilde{\mathbf{E}}$ which is smaller by a small factor v/c than the interaction with the alternating magnetic field ($\beta_0 \tilde{\mathbf{H}}$), and can give rise only to transitions which are much weaker than in paramagnetic resonance.

A general investigation of the singularities of the combined resonance can be made if the terms causing the coupling between the configurational and spin motions are small and can be regarded as a perturbation. Then in the zeroth approximation Hamiltonian

$$H_0 = \sigma_0 f_0(\hat{\mathbf{k}}) + \frac{1}{2} \beta_0 (\boldsymbol{\sigma} g(0) \mathbf{H}) \quad (2.13)$$

the configurational and spin motions can be separated and the eigenfunctions can be chosen in multiplicative form. If we confine ourselves in $f_0(\hat{\mathbf{k}})$ to quadratic terms, which is usually sufficient, then the equal-energy surfaces are spheres or ellipsoids, and the eigenfunctions are Landau functions. The second term in (2.13) determines the spin function. It can always be reduced, by transforming the coordinate frame, to the diagonal form $(1/2) \beta_0 g(\Omega) \sigma_Z \mathbf{H}$, where $g(\Omega)$ is determined by the orientation of \mathbf{H} ; we shall assume in the present section that this transformation has been made.

It is convenient to carry out canonical transformation of all the operators

$$\hat{A} \rightarrow e^T \hat{A} e^{-T} \quad (2.14)$$

with the aid of an operator T such that all the terms that are off-diagonal in the spin vanish as a result of the transformation from the total Hamiltonian $H = H_0 + H_1$. Then the terms proportional to H_1 in the diagonal part, which lead to corrections to the energy

* $[\mathbf{E}, \hat{\mathbf{k}}] = \mathbf{E} \times \hat{\mathbf{k}}$.

levels but which do not influence the combined resonance intensity, can be neglected in the defined approximation. The transformed Hamiltonian then coincides with H_0 .

In first order in H_1 , the matrix elements of the operator T are equal to

$$\langle n' | T | n \rangle = \frac{\langle n' | H_1 | n \rangle}{E_{n'} - E_n} \quad (2.15)$$

for the states n and n' corresponding to different spin orientations; all the matrix elements which are diagonal in the spin can be set equal to zero. In the same approximation, the transformed velocity operator is

$$\mathbf{v} = \frac{1}{i\hbar} \{ [\mathbf{r}, H_0] + [\mathbf{r}, H_1] + [T[\mathbf{r}, H_0]] \}. \quad (2.16)$$

The first term in (2.16) describes cyclotron resonance, and the last two combined resonance.

The indices n in (2.15), which number the states, incorporate four quantum numbers: three orbital (discrete oscillator quantum number n and two continuous numbers k_x and k_z ; see, for example, [6]) and one spin number σ . Using the usual properties of motion in a homogeneous magnetic field, we can readily verify that the operators H_1 , $\mathbf{r} \times \mathbf{H}_0$, and T are diagonal in k_x and k_z . In addition, the operator $\mathbf{r} \times \mathbf{H}_0$ can be broken up into three parts which act on the Landau functions and lead either to conservation of n or to an increase or decrease of n by unity while the remaining quantum numbers remain unchanged; the corresponding parts of \mathbf{r} will be denoted by r_α ($\alpha = 0, -1, +1$). Using this notation, we can easily verify that for transitions with change of the spin state

$$\langle n' | [T, [r_\alpha, H_0]] | n \rangle = \frac{\alpha \hbar \omega_c(\Omega)}{E_n - E_{n'} + \alpha \hbar \omega_c(\Omega)} \langle n' | [r_\alpha, H_1] | n \rangle, \quad (2.17)$$

where $\omega_c(\Omega)$ —cyclotron resonance frequency for the chosen orientation of \mathbf{H} . Thus, the matrix elements of the two operators responsible for the excitation of the combined resonance are proportional to each other, and to obtain a qualitative picture of the effect it is sufficient to consider only the first operator.

Whereas the form of the equal-energy surface is determined predominantly by the operator H_0 , the intensity of the combined resonance is determined by the operator H_1 , which, as a rule, contains in the symmetrized combinations $\hat{\mathbf{k}}$ components raised to a higher power (which we denote by s) than H_0 . Therefore the angular dependences of combined resonance are usually less symmetrical than the equal-energy surfaces.

As can be seen from (2.16), the part of the operator \mathbf{v} responsible for the combined resonance is a form of degree $s - 1$ in the component $\hat{\mathbf{k}}$. Taking into account the known selection rules for the momentum matrix elements, we can easily see that the combined-resonance spectrum should consist of $2s - 1$ bands (pure spin transition) and $2(s - 1)$ bands corresponding to spin flip with simultaneous

change of n [by $\pm 1, \pm 2, \dots, \pm(s - 1)$]. The higher the order of the perturbation H_1 in the effective-mass method appears, the richer the combined-resonance spectrum; at the same time, however, the intensities decrease rapidly and experimental observation of the individual bands becomes accordingly more difficult.

The individual bands correspond to different combinations of the operators $\hat{\mathbf{k}}_\alpha$; they therefore have a different dependence on the orientation \mathbf{H} and on the quantum numbers. This leads to a difference in the angular dependences of the combined-resonance intensity as a function of the orientation of \mathbf{H} , and also to different dependences on H , on the electron concentration (in the presence of degeneracy), and on the temperature (for a nondegenerate electron gas). Along with the monotonic dependence of the intensity of combined resonance on H in the presence of degeneracy, oscillations of the de Haas-van Alphen type appear. The excitation of combined resonance is possible both when $\tilde{\mathbf{E}} \perp \mathbf{H}$ (transverse resonance) and when $\tilde{\mathbf{E}} \parallel \mathbf{H}$ (longitudinal resonance).

The entire analysis of combined resonance, given above, was based on the assumption that the corrections to the Hamiltonian H_0 , which give rise to the combined resonance, are small. For crystals with inversion centers, this reduces to the requirement that the corrections to the g -factor, necessitated by its dependence on \mathbf{k} , be small compared with the g -factor itself; this condition is in practice always satisfied in semiconductors. The corresponding criterion is much more stringent in semiconductors without inversion centers, where it is required that the spin-orbit divergence of the bands $\delta(k)$, at quasimomenta on the order of k_{char} , be much smaller than the cyclotron energy $\hbar \omega_c(\Omega)$ (or the Zeeman energy $\hbar \omega_s(\Omega) = |g(\Omega)| \beta_0 H$); when these quantities become of the same order of magnitude, the resonant frequencies common to all the electrons vanish, and the absorption bands should broaden greatly. This criterion, which imposes an upper bound on k_{char} , simultaneously limits, in the case of a fixed operating frequency, the carrier density for the degenerate electron gas, and the temperature for the nondegenerate gas.

It is easy to estimate the ratio of the matrix elements of the velocity operator for combined and cyclotron resonance. According to (2.16), its order of magnitude is

$$\frac{v_{\text{CoR}}}{v_{\text{CyR}}} \sim \frac{H_1(k_{\text{char}})}{H_0(k_{\text{char}})} \sim \frac{H_1(k_{\text{char}})}{E_{\text{char}}}. \quad (2.18a)$$

As was just noted, pronounced resonance is observed when

$$|H_1(k_{\text{char}})| < \hbar \omega_c(\Omega) \sim \hbar \omega_s(\Omega),$$

and therefore

$$\frac{v_{\text{CoR}}}{v_{\text{CyR}}} < \frac{\hbar \omega_s(\Omega)}{E_{\text{char}}}. \quad (2.18b)$$

The quantity on the right side is of the order of unity

only in the case of the quantum limit, when $k_{\text{char}} \sim k_H$; in all other cases it is always smaller than unity.

To conclude this section we shall dwell briefly on the widths of the combined resonance bands. We can introduce two relaxation times: τ —the relaxation time within each of the two spin subsystems, and τ_S —the spin relaxation time. If they are of the same order of magnitude, then the widths of all the resonance absorption bands are comparable with one another and are of the order of τ^{-1} on the frequency scale. Usually, however, $\tau \gg \tau_S$, and the paramagnetic resonance band, which has a width $\sim \tau_S^{-1}$, is much narrower than the cyclotron-resonance band, which has a width $\sim \tau^{-1}$. This raises the question: what will be the widths of the different combined-resonance bands?

Naturally, the bands corresponding to the combination transitions with frequencies $n\omega_C(\Omega) \pm \omega_S(\Omega)$ will have a width $\sim \tau^{-1}$, since they are accompanied by change in the number of the cyclotron orbit by $n \neq 0$.

The pure spin-transition band occupies a special position. To verify this, it is convenient to consider the case when the operator H_1 contains \hat{k}_α linearly; consequently \mathbf{v}_S , which is the relativistic part of \mathbf{v} [see (2.16)], does not contain \hat{k}_α and depends exclusively on the spin operators. If we neglect further the spin interactions in the total Hamiltonian of the system, then the Hamiltonian can be written in the form $H = H_R + H_S$, where H_R is the configuration part of the Hamiltonian, which includes the interaction with the scatterers, and H_S is the spin Hamiltonian which enters into (2.13). Using the fact that H_R commutes with \mathbf{v}_S and H_S , we can easily transform the well-known formula for the real part of the conductivity:

$$\begin{aligned} \sigma_{\alpha\beta}(\omega) &\sim \text{Re} \int_0^\infty dt e^{i\omega t} \langle [e^{iH_1} v_\alpha^a e^{-iH_1}, v_\beta^b] \rangle \\ &= \text{Re} \int_0^\infty dt e^{i\omega t} \langle [e^{iH_S} v_\alpha^a e^{-iH_S}, v_\beta^b] \rangle \sim \delta(\omega - \omega_S). \end{aligned} \quad (2.19)$$

Consequently, the width of the band of the pure spin

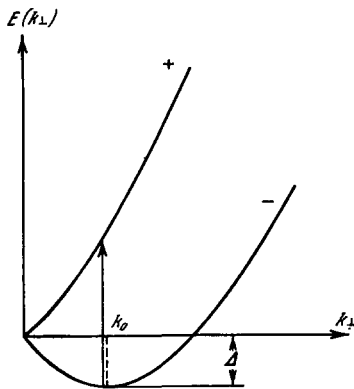


FIG. 1. Plot of $E(k_\perp)$ for semiconductors with extremum loop. Δ — depth of loop, k_0 — radius of loop. The signs + and — indicate the branches of the dispersion law (3.2). The arrow designates transitions corresponding to combined resonance of carriers with extremely low energy.

transition is determined by corrections to the levels of order H_1 , which have not yet been accounted for here, and by the spin relaxation. No analogous analysis was made so far for the more complicated case when \mathbf{v}_S depends on $\hat{\mathbf{k}}$. However, an approximate theory, based on a generalization of the Karplus-Schwinger method to include the case of two relaxation times, leads to the conclusion that in the general case the spin band has a width $\sim \tau_S^{-1}$ at arbitrary τ .

It must be noted that the entire analysis made in this section of the combined resonance picture is based on a Hamiltonian which does not include scattering, and is therefore valid when $\omega\tau, \omega\tau_S \gg 1$.

3. COMBINED RESONANCE WITH BAND CARRIERS IN CRYSTALS OF DIFFERENT SYMMETRY. DISCUSSION OF FIRST EXPERIMENTAL RESULTS

We consider now the distinguishing feature of combined resonance with band carriers for several basic types of band structure, corresponding to the most thoroughly investigated semiconductor groups.

As follows from Sec. 2, combined resonance should be the most intense in crystals without an inversion center, in which the spin-orbit divergence of the bands appears already in the first order in k . Among these, apparently, the most convenient object of investigation are semiconductors with loops of extrema, such as CdS; a discussion of the prevalence of band structures of this type, the values of the parameters, etc., is contained in [7].

In the hexagonal modification of crystals of the CdS type with symmetry C_{6v} , the matrix Hamiltonian of the band electrons has near $k_0 = 0$ the form

$$\begin{aligned} H(\hat{\mathbf{k}}) &= \sigma_0 (A\hat{k}_\perp^2 + B\hat{k}_z^2) + \alpha [\sigma_x \hat{k}_x + \sigma_y \hat{k}_y] \\ &+ \frac{\beta_0}{2} \{g_\perp (\sigma_\perp \mathbf{H}) + g_\parallel \sigma_z H_z\}, \end{aligned} \quad (3.1)$$

where Oz is oriented along the hexagonal axis, $k_\perp^2 = k_x^2 + k_y^2$, and $\sigma_\perp = (\sigma_x, \sigma_y)$. The constant α determines the magnitude of the spin-orbit divergence of the bands. The law of electron dispersion corresponding to the Hamiltonian (3.1) [2,8,9] is

$$E_\pm(\mathbf{k}) = Ak_\perp^2 + Bk_z^2 \pm \alpha k_\perp. \quad (3.2)$$

The energy minimum $E_{\text{min}} = -\Delta = -\alpha^2/4A$ is attained for the lower sign in (3.2) (we assume for concreteness that $\alpha > 0$) on a circle (extremum loop) with radius $k_0 = \alpha/2A$, lying in the plane $k_z = 0$. A plot of the energy as a function of k_\perp is shown in Fig. 1. At small energies, $|E - E_{\text{min}}| < \Delta$, the equal-energy surfaces have a toroidal form.

When the carriers are concentrated at the bottom of the band, $k_{\text{char}} \approx k_0$ and the divergence of the bands is $\approx \delta(k_0) = 4\Delta$. To the contrary, at characteristic energies that are large compared with Δ , we have $\delta(k_{\text{char}}) \sim 4\sqrt{E_{\text{char}}\Delta}$. Consequently, the situation analyzed in Sec. 2, where $\delta(k_{\text{char}}) \ll \hbar\omega_S$ and the terms $\sim \delta(k_{\text{char}})$ can be regarded as a perturbation,

occurs in the case of semiconductors with an extremum only in sufficiently strong magnetic fields which break the spin-orbit coupling.* For example, when $\delta(k_{\text{char}}) \sim 4 \times 10^{-5}$ eV ($E_{\text{char}} \sim 10^{-4}$ eV, $\Delta \sim 10^{-6}$ eV—this apparently corresponds approximately to a value of Δ in certain crystals of this group) the operating frequency of the apparatus should satisfy the condition $\nu = \omega/2 \gg 10^{10}$ cps, and the magnetic field for $g \approx 2$ must satisfy the condition $H \gg 3000$ Oe. At larger values of Δ , these criteria will be much more stringent and, for example, even when $\Delta \sim 10^{-5}$ eV they correspond to a transition into the infrared region of the spectrum.

If the criterion $\delta(k_{\text{char}}) \ll \hbar\omega_s$ is satisfied, then a single combined-resonance band at a frequency ω_s should be observed. Using (2.18a), we can readily verify that $(v_{\text{CoR}}/v_{\text{CyR}})^2 \sim \Delta/E_{\text{char}}$. At the same time, an analogous ratio for paramagnetic and cyclotron resonance is of the order of $(g\lambda_0/r_{\text{char}})^2$. Therefore the ratio of the intensities is

$$\frac{I_{\text{CoR}}}{I_{\text{CyR}}} \sim \frac{\Delta}{E_{\text{char}}} \left(\frac{r_{\text{char}}}{g\lambda_0} \right)^2 \sim \frac{\Delta mc^2}{(\hbar\omega_s)^2}. \quad (3.3)$$

When $\Delta \sim 10^{-6}$ eV, $\hbar\omega_s \sim 10^{-4}$ eV, and $m \sim 0.1m_0$, this ratio is $\sim 10^7$; consequently, for a similar band structure the combined resonance is stronger than the paramagnetic resonance by many orders of magnitude. A detailed theory of combined resonance in semiconductors with extremum width in strong magnetic fields is given in^[10].

Combined resonance in semiconductors with an extremum loop is of interest not only because of its high intensity, but also because when H is oriented along the symmetry axis the Schrödinger matrix equation can be solved accurately^[11], so that the picture of combined resonance can be investigated in a wide range of H .

The exact energy spectrum of the system consists of two branches, which can be set in correspondence with the two branches of the dispersion law. Two transitions are possible from each state of the lower branch into the states of the upper branch; the frequency of the transition depends on the quantum number of the initial state; therefore, as a rule, the combined-resonance spectrum should have no structure and should be resolved only in a few limiting cases.

If Δ is large, the magnetic fields are not too large, and the majority of the carriers is concentrated at the bottom of the band, then the combined resonance is essentially an interband absorption of the carriers with transition between two spin-conjugate bands; in Fig. 1 these transitions are indicated by an arrow. The absorption is located near the frequency $\omega = 4\Delta/\hbar$

and consists of a series of peaks spaced $2\omega_{c\perp} = 4Ak_H^2/\hbar$ apart. The strength of the combined-resonance oscillator is in this case very high and coincides with the strength of the cyclotron-resonance oscillator; at the same time, combined resonance is easier to observe than cyclotron resonance, since the quasiclassical cyclotron-resonance frequency, which is equal to^[12]

$$\omega_c = \frac{eH}{c} \cdot \frac{2\pi}{\hbar^2} \cdot \frac{\partial S_-}{\partial E_-} = \omega_{c\perp} \cdot \frac{k_{\perp} - k_0}{k_{\perp}}, \quad (3.4)$$

vanishes when $k_{\perp} = k_0$ (S_- —area of the intersection between the equal-energy surface E_- and the plane $k_z = \text{const}$).

To the contrary, if $E_{\text{char}} \gg \Delta$ and the magnetic field breaks the spin-orbit bond, two bands will appear in the combined-resonance spectrum. One of them, discussed above, will correspond to the frequency $\omega_{s\parallel} = |g_{\parallel}| \beta_0 H/\hbar$; the other, which is one of the frequencies resulting from the combination of $2\omega_{c\perp}$ with $\omega_{s\parallel}$ (which depends on the ratio of the parameters), is weaker than the first band by a factor $\sim (\delta(k_{\text{char}})/\hbar\omega_{c\perp})^4$.

We note that the case of large Δ was considered^[13] also for H oriented perpendicular to the symmetry axis; since the exact solution cannot be obtained, a quasiclassical method was used. Unlike the majority of other effects in combined resonance, the region near the central section makes a small contribution; inasmuch as the frequency of the combined resonance furthermore depends strongly on the quantum numbers when $\hbar\omega_s \ll \Delta$, the absorption should extend over a broad band.

Unfortunately, the resonant properties of those semiconductors in which high combined-resonance intensity should come into play in conjunction with interesting peculiarities of cyclotron resonance^[1] have not been investigated experimentally at all. The results of the only investigation^[14] of cyclotron resonance in n-CdS is in contradiction with the later investigations of other effects.

The second theoretically-investigated type of band structure without an inversion center is that of crystals of the n-InSb type^[15]. In such crystals, if we confine ourselves to terms that are cubic in \hat{k}_{α} , the matrix Hamiltonian is of the form

$$H_0 = \frac{\hbar^2 \hat{k}^2}{2m} + \frac{g\beta_0}{2} (\sigma H), \quad H_1 = \delta_0 (\sigma \hat{\alpha}), \quad (3.5)$$

where

$$\hat{\alpha}_x = \hat{k}_y \hat{k}_x \hat{k}_y - \hat{k}_z \hat{k}_x \hat{k}_z, \quad (3.6)$$

and \hat{k}_y and \hat{k}_z are obtained from \hat{k}_x by cyclic permutation of the indices; the cubic axes are chosen to be the coordinates.

Inasmuch as H_1 is cubic in \hat{k}_{α} , the intensity of the combined resonance should be appreciably lower than in semiconductors with an extremum loop; in strong fields the spectrum should contain, besides the spin-resonance frequency, also four combination

*We are referring, naturally, not to the breaking of the intratomic spin-orbit bonds, with energy on the order of an electron volt, but to the satisfaction of the criterion $\delta(k_{\text{char}}) \ll \hbar\omega_s$, which ensures an appreciable autonomy of the configurational and spin motions of the band carriers.

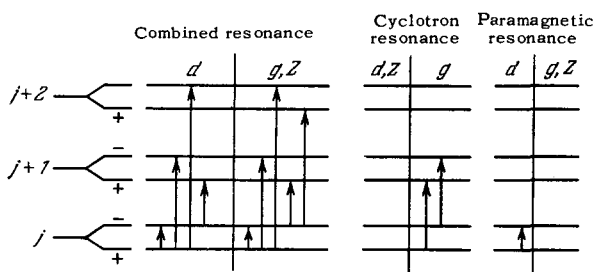


FIG. 2. Electron energy level scheme of InSb in a magnetic field. The arrows indicate the transitions corresponding to various resonances; it is assumed that the combined resonance is due to the term H_1 from (3.5). The letters designate the types of polarization: longitudinal (Z), right-hand (d), and left-hand (g) circular.

frequencies; the transition scheme for InSb is shown in Fig. 2. The combined-resonance intensity should be strongly anisotropic; typical angle diagrams are shown in Fig. 3. The intensities of all the bands were calculated in [15] for many limiting cases, together with the dependence of the intensities on the temperature, electron density, and H ; the intensity oscillations in the presence of degeneracy were also investigated.

An estimate of δ_0 , obtained for InSb on the basis of the Kane model [16], yields $|\delta_0| \approx 2 \times 10^2$ atomic units. This value of $|\delta_0|$ for $\nu = 2.4 \times 10^{10}$ cps, leads to a concentration limit of observation of spin resonance $N_{lim} \sim 6 \times 10^{15} \text{ cm}^{-3}$.

Spin resonance of band electrons was observed in InSb for the first time by Bemski [17]. He was able to observe resonance at $\nu = 2.4 \times 10^{10}$ cps up to concentrations $N \approx 3 \times 10^{15} \text{ cm}^{-3}$; at higher concentrations, owing to the sharp broadening of the band, starting with approximately $N \approx 2 \times 10^{15} \text{ cm}^{-3}$, it was impos-

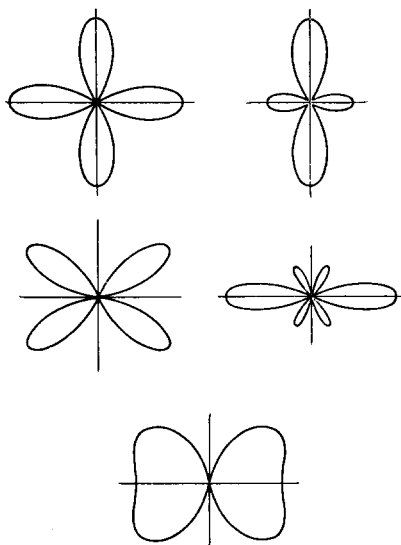


FIG. 3. Typical angle diagrams of the combined-resonance intensity for crystals of the InSb type. The coupling of the configurational and spin motions is realized by the operator H_1 from (3.5).

sible to observe the resonance. Satisfactory agreement between the theoretical and experimental values of N_{lim} indicates the correctness of the estimate of $|\delta_0|$. At the same time, for this value of $|\delta_0|$ and for the values of concentrations and temperatures corresponding to Bemski's measurements, the increase of combined-resonance intensity at the antinode of the electric component of the high-frequency field, compared with the intensity of the paramagnetic resonance at the antinode of the magnetic component, is estimated theoretically to be approximately four orders of magnitude; inasmuch as the dimensions of the samples are usually approximately 0.1 of the wavelength, even if the sample is placed in the antinode of the magnetic field, the electric excitation cannot be excluded. Therefore it was suggested in [15] that Bemski actually observed a superposition of combined and paramagnetic resonances.

This assumption was confirmed in later experiments by Bratashevskii, Galkin, and Ivanchenko [18]* and by Bell [19]. They observed a narrow spin resonance band (~ 10 – 20 Oe) against the background of a broad cyclotron-plasma resonance band and proved directly, by displacing the sample in the resonator, that the electric excitation of the spin transitions prevails over the magnetic excitation. It can therefore be assumed that in these investigations the combined resonance with the band carriers was observed experimentally. Figure 4 shows by way of an illustration the curves obtained by Bell.

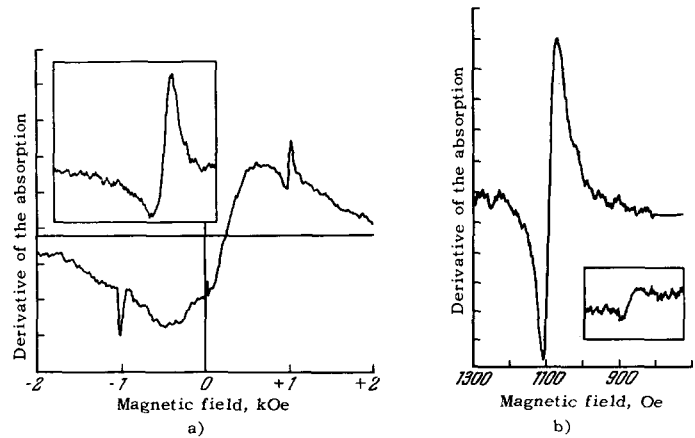
At the same time the impurity scattering in these experiments, which were performed at liquid-helium temperature, was so strong that the criterion $\omega\tau \gg 1$ was greatly deviated from, as can be seen from the extremely smeared cyclotron-resonance curves. We can therefore expect appreciable deviations from the predictions of the theory, particularly in the angle diagrams, which are determined by the symmetry of the quantum states.

In both experimental works [18,19] it was established that the combined resonance is isotropic at the frequency ω_S at all polarizations. Although there is no systematic theory of combined resonance under the conditions $\omega\tau \lesssim 1$ and $\omega\tau_S \gg 1$ at present, we can show that strong scattering should smooth out the angle diagrams; nonetheless, it apparently should not lead to complete isotropy, at any rate so long as the inequality $\hbar/\tau \ll \zeta$, which was satisfied in [18,19], is still valid ($\zeta =$ Fermi energy).

Worthy of attention is still another circumstance. A peculiarity of InSb, governing the characteristic values of several parameters of its band structure ($m = 0.013 m_0$, $g = -51$, etc.) is the small width of the forbidden band E_g (which slightly exceeds

*The results were partially reported by Yu. A. Bratashevskii at the Ninth All-union Conference on Low Temperature Physics in Leningrad, June 1962.

FIG. 4. Resonant absorption of electrons in InSb. a) Electric-dipole absorption. On the smeared edge of cyclotron resonance, near 1 kOe, one can see at both orientations of the magnetic field combined-resonance peaks corresponding to pure spin transition; in the insert, one of the peaks is shown on an enlarged scale. b) Magnetic-dipole absorption. In one of the polarizations one can see the paramagnetic resonance band while the second polarization (insert) does not contain this band.



0.2 eV). This makes it necessary to consider, besides the operator H_1 from (3.5), also the term H'_1 due to the dependence of the g -factor on \mathbf{k} . Indeed, although H'_1 is a quantity of higher order of smallness in the quasimomentum (it is proportional to $k_H^2 k_{\text{char}}^2$), it contains nevertheless a term of the type $(\boldsymbol{\sigma} \cdot \mathbf{k})(\mathbf{H} \cdot \mathbf{k})$, which is due to the "interaction" of the nearest bands, whereas δ_0 is determined predominantly by the contribution of the upper bands. This term can be readily estimated at

$$H'_1 \sim \frac{\hbar^2}{2m} \frac{\hbar \omega_s}{E_g} (\boldsymbol{\sigma} \hat{\mathbf{k}}) \left(\frac{\mathbf{H}}{H} \hat{\mathbf{k}} \right). \quad (3.7)$$

Comparison with H_1 makes it immediately possible to estimate the relative contribution of both operators to the velocity matrix elements:

$$\frac{v_{H_1}}{v_{H'_1}} \sim \frac{\delta(k_{\text{char}}) E_g}{\hbar \omega_s E_{\text{char}}}. \quad (3.8)$$

When $N \sim 10^{14} \text{ cm}^{-3}$ and the frequencies have the values assumed in [18, 19], this quantity is of the order unity and the contribution of the term H'_1 should be taken into account, something not done in earlier work (see note added in proof at the end of the article). Inasmuch as H'_1 from (3.7), unlike H_1 , is a spherical invariant (and not cubic), the absorption caused by it should be isotropic. It is easy to verify that when $\omega\tau$ and $\omega\tau_s \gg 1$, H'_1 gives rise to transitions at one of the combination frequencies in longitudinal polarization and to pure spin transitions in one of the circular transverse-resonance polarizations, but does not lead to absorption in the other polarization. When $\omega\tau < 1$ and $\omega\tau_s \gg 1$, H'_1 apparently can explain the isotropy of the absorption in the longitudinal and one of the circular polarizations, but not the equality of the absorption in both circular polarizations, which was established by Bell [19]. Further investigations are therefore necessary here.

Increasing the temperature leads to weakening of the impurity scattering, to an increase in $\omega\tau$, and to a narrowing of the cyclotron resonance band. At liquid oxygen temperature, Bratashevskiĭ, Galkin, and

Ivanchenko [18] succeeded in compensating the cyclotron absorption in the longitudinal polarization to a considerable degree, and in observing four new absorption bands excited by the electric component of the field. These bands have appreciable anisotropy and are located in the regions 4000–7000 Oe (Fig. 5). They advanced the opinion that the bands observed by them are the four remaining combined-resonance bands.

However, strict identification of the observed bands, and elimination of the other possible interpretations, are made extremely difficult by the following circumstance. Owing to the small effective mass of the electrons ($m = 0.013m_0$), the plasma effects in n -InSb are very large, and for $N \approx 10^{14} \text{ cm}^{-3}$ the position of the cyclotron-resonance band is shifted by the plasma interaction by one order of magnitude into the region of large magnetic fields (from ~ 300 to ~ 3000 Oe), leading to a realignment of the entire absorption curve. At the same time, the elimination of the distortion introduced by the plasma effects, by recalculating the experimental data, is made difficult by the influence of the skin effect—the skin depth is of the order of the spherical samples. Therefore the

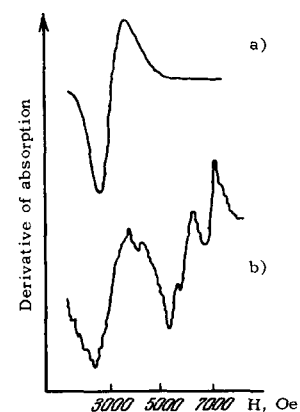


FIG. 5. Resonance absorption of electrons in InSb. a) Magneto-plasma resonance in transverse polarization; b) magnetoplasma resonance and four absorption bands in longitudinal polarization.

question of the nature of the observed bands and the possibility of their interpretation as being for combined-resonance bands shifted by the plasma interaction from the 150–500 Oe region (theoretical position) into the region 4000–7000 Oe still awaits a final solution.

Summarizing the comparison of the theoretical and experimental results on n-InSb, we must conclude that the existence of combined resonance has been established unambiguously; at the same time, it is necessary both to generalize a theory to include new cases (strong scattering $\omega\tau \lesssim 1$, allowance for plasma effects), and to carry out new experiments under conditions satisfying the criteria of the already existing theory. Among the semiconductors with inversion center, greatest interest is attached to Ge and Si, as being most suitable for resonance investigations.

The theory of combined resonance of electrons in germanium and silicon was constructed by Boiko^[20], who showed that in Si there should occur a single band at a frequency ω_S , and in Ge three bands at frequencies ω_S and $\omega_C \pm \omega_S$. An estimate of the probabilities of the transitions has shown that in both cases the intensities of combined and paramagnetic resonances should be comparable in order of magnitude. Inasmuch as in semiconductors with inversion center the combined resonance is the result of the dependence of the g -factor on \hat{k} , it should be strongest in the presence of nearby bands, when the deviation of g from a constant value occurs particularly early. We encounter a similar situation in p-Ge and p-Si crystals subjected to deformation, which lowers the symmetry and lifts the degeneracy of the bands of heavy and light holes in $k_0 = 0$; in such cases the distance between the split bands Δ_ϵ is usually of the order of several hundred eV. This interesting situation was investigated by Gurgenshvilii^[21] on the basis of the theory of Pikus and Bir^[22]; the intensities and the angular dependence of combined resonance are expressed in his paper directly in terms of the Luttinger parameters^[23], which are known from other experiments.

The order of magnitude of the effects obtained by him can be readily estimated in the following fashion. From dimensionality considerations it is clear that the term in the g -factor which is quadratic in k is of the order of $\hbar^2 k_{\text{char}}^2 / m \Delta_\epsilon$. Consequently, the term in the velocity operator, responsible for the combined resonance, is of the order $(\hbar k_{\text{char}} / m) \times (\beta_0 H / \Delta_\epsilon)$, and the matrix element of the coordinate is of the order $\hbar^2 k_{\text{char}} / m \Delta_\epsilon$. Therefore

$$\frac{I_{\text{CoR}}}{I_{\text{CyR}}} \sim \frac{mc^2 E_{\text{char}}}{\Delta_\epsilon^2}. \quad (3.9)$$

When $E_{\text{char}} \approx 3 \times 10^{-4}$ eV and $\Delta_\epsilon \approx 10^{-2}$ eV, this ratio is of the order of 10^6 .

In undeformed germanium and silicon crystals, as

is well known, the levels of the holes in a magnetic field are not equidistant at small quantum numbers (the quantum region), owing to the fourfold degeneracy of the bands in $k_0 = 0$; the systematics of the quantum levels in this situation was developed by Luttinger^[23], and a detailed theory of the quantum transitions was given in subsequent works (Khutsishvili et al^[24]). In^[24] it is shown that in the quantum region practically all the transitions are accompanied by a change in the spin state, and these types of transitions whose properties in the quasi-classical region can be attributed to combined resonance ($a^\pm(n) \leftrightarrow b^\pm(n+1)$ transitions in the notation of^[23]) are excited in longitudinal polarization in the spherical-band approximation. In the approximation used in^[24], the intensity of combined resonance decreases monotonically with increasing n ; however, an inclusion of terms $\sim \hbar \hat{k}_\alpha \hat{k}_\beta$ in the Hamiltonian will cause the combined-resonance intensity first to pass through a minimum and then to grow again in the region of large n .

In conclusion let us dwell on the interesting results of Smith, Galt, and Merritt^[25], who observed the combination frequencies $\omega_C \pm \omega_S$ in the spectra of Bi and Sb. In these crystals with small E_g and large g -factor, the dependence of g on \hat{k} should be appreciable, and apparently in this connection the opinion was advanced^[19] that the effect observed in^[25] has the same nature as combined resonance at the frequency ω_S in InSb. However, bismuth and antimony are metals with strongly pronounced skin effect, and in the skin layer the high-frequency electric field is much weaker than the magnetic field (by a factor on the order of the ratio of the thickness of the skin layer to the wavelength^[26]); therefore the conditions for the electric excitation of the spin transitions are less favorable here than in n-InSb. Yet it is precisely under conditions of strong skin effect, as noted by Azbel^[27], that a high-frequency magnetic field with strong spatial inhomogeneity will excite, besides the pure spin transitions, also transitions at combination frequencies. The polarization of the transitions, established by Smith et al, indicates that the bands they observed are more likely magnetic-dipole and are due to the mechanism of^[27].

4. COMBINED RESONANCE WITH BOUND CARRIERS (GENERAL ANALYSIS)

As was already noted in Sec. 1, the high intensity of the combined resonance with band carriers leads to a change in the conditions for the excitation of spin resonance on local centers, namely the possibility of combined resonance with the bound carriers. We shall consider below predominantly centers with large radius, so that we can compare directly the combined resonances with them and with band carriers by constructing the theory in general terms,

and thus separate the singularity due to the transition of the electron into the bound state. As can be seen from the preceding section, the oscillator strength f of combined resonance with the band carriers can be very high, reaching values on the order of unity. For fields H that break the spin-orbit coupling, f can be readily estimated with the aid of (2.18a), by recognizing that the oscillator strength of cyclotron resonance is of the order of $E_{\text{char}}/\hbar\omega_c$. For example, for crystals without an inversion center

$$f \sim \frac{\delta^2(k_{\text{char}})}{E_{\text{char}}\hbar\omega_c}. \quad (4.1)$$

It is interesting to note that the oscillator strength is proportional to H^{-1} so long as k_{char} does not depend on H .

It is easy to explain the cause of the high values of f . As is well known for the band electron there is, besides the oscillator strength for the transition to other bands, also a nonvanishing oscillator strength for the transition "into itself," which is equal to m_0/m [28]; it is precisely this oscillator strength which causes the interband absorption of light by free carriers and the cyclotron absorption. The oscillator strength for the transition "into itself," possessed by the Schrödinger band electron, is shared, on going over to the relativistic electrons and when the number of bands is doubled, by two bands—transition "into itself" and transitions into the spin-conjugate band; the latter oscillator strength is, roughly speaking, the source of the combined resonance.

At the same time, for the bound states, the oscillator strength, both for the transition "into itself" and for the transition to other states that are degenerate relative to the usual state, is always equal to zero because of the finite radius of the state R . Consequently, the nonzero values of f will always appear only in higher orders in the magnetic field H , which splits the levels. The expansion parameter will be $\hbar\omega_S/E_i \sim (k_H R)^2$, where E_i is the potential of the center, and is a characteristic quantity for the distances between the successive levels, and f , unlike (4.1), will contain only the direct powers of H (at any rate, so long as $\hbar\omega_S \ll E_i$). Consequently, other conditions being equal, the combined resonance with the bound carriers should be much weaker than with the band carriers (É. I. Rashba, paper at All-union Symposium on Solid State Theory and New Methods of Quantum Statistics, Odessa, May, 1961).

We now consider in greater detail [29] the structure of the matrix element of the coordinate r for combined resonance, and confine ourselves first to the local level produced at the bottom of a simple band. More accurately, we assume that there is no multi-valley structure, and likewise no spin-orbit splitting of the band at the point k_0 , at which the bottom of the band is located (usually $k_0 = 0$), and we likewise assume double degeneracy in k_0 with

account of the spin; in semiconductors without an inversion center, to which we confine ourselves temporarily, the bands in the vicinity of k_0 will diverge slightly.

We shall now verify that

$$r \sim \frac{\hbar\omega_S}{E_i} \frac{\delta(k_R)}{E_i} R, \quad k_R = \frac{\pi}{R}. \quad (4.2)$$

The last factor in (4.2), R , is the maximum value of the matrix element of the transition—the radius of the center; the first two factors are small and are due to an account of the perturbations that make the combined resonance possible. Indeed, the second factor takes into account the effect of band divergence, which in the model assumed here, is the only reflection of the existence of spin-orbit coupling.

In the case of a simple band, the main level of the impurity center is doubly degenerate as a result of T -symmetry at $H = 0$ (when spin is taken into account); the two wave functions belonging to it can be denoted ψ and $K\psi$. Using the properties of the operator K , we easily verify [5] that

$$(K\psi, r\psi) = (Kr\psi, K^2\psi) = -(Kr\psi, \psi) = -(K\psi, r\psi) = 0. \quad (4.3)$$

Therefore, the matrix element of the coordinate differs from zero only in first order in H , and this causes the appearance of the first factor in (4.2).

Let us note now the circumstances under which the small factors can vanish from (4.2). The first factor vanishes for states with angular momentum $J > 1/2$ and transitions with variation of the modulus of the magnetic quantum number M , since the initial and final states are not conjugate relative to time inversion in this case. Such a situation is realized with $J = 3/2$ for acceptors in degenerate bands (of the type p -Ge, Si, InSb [30]). In the same case, the second factor also vanishes, since the spin-orbit divergence of the bands at the symmetry point usually exceeds E_i (or else is a quantity of this order). It must be borne in mind, however, that in the case in question the second factor performs still another role. The point is that in the presence of an inversion center the electric-dipole transitions between the different states within a single term are forbidden, and the operator that causes the spin-orbit divergence of the bands is simultaneously the only term in the Hamiltonian which is odd relative to inversion. Therefore, for acceptor centers of the type indicated, if we neglect $\delta(k_R)$ we can obtain a nonvanishing combined-resonance intensity only by taking into account other odd terms in the Hamiltonian of the effective-mass method; we shall discuss this in greater detail in the next section.

Finally, the matrix element r can increase appreciably in the presence of nearby levels, when the denominators in (4.2) will contain in place of E_i an essentially smaller quantity; this is possible in a multivalley structure, for excited levels, etc.

It is easy to see that f is proportional to H when r does not depend on H , and is proportional to H^3 when r is proportional to H , thus differing noticeably from (4.1).

5. COMBINED RESONANCE WITH LOCAL CENTERS OF VARIOUS TYPES

Let us consider now in greater detail several special cases. If we apply (4.2) to semiconductors with extremum loops and assume for the parameters values that are apparently close to those realized in CdS, CdSe, and others ($E_i \sim 3 \times 10^{-2}$ eV, $\alpha \sim 10^{-10}$ eV-cm), then for $\nu \approx 10^{11}$ sec $^{-1}$ we obtain $r \sim 10^{-10}$ cm, which exceeds λ_0 .*

Calculations made by a variational method for semiconductors with extremum loops^[29] lead in the region of weak fields to a result close to (4.2), and in the region of strong fields ($\hbar\omega_S \gg E_i$) to the same intensities as for the band carriers^[10]. In intermediate fields, $\hbar\omega_S \sim E_i$, the intensity as a function of H goes through abrupt maxima, which arise when the terms cross; the corresponding absorption frequencies lie in the infrared region of the spectrum.

As was shown in Sec. 4, the highest combined resonance intensities should be expected for acceptor centers with large radius, the ground state of which has fourfold degeneracy. The situation is most amenable to analysis in p-InSb, for the absence of the inversion centers in the crystals causes the Hamiltonian of the band holes to contain terms that are odd and cubic in k ; this makes it possible to construct a purely macroscopic theory within the framework of the effective-mass method^[32]. Inasmuch as the cubic terms in InSb are nonrelativistic, the relative magnitude compared with the quadratic terms is $\sim (a/R)$, where a is the lattice constant, and consequently for transitions with change in $|M|$ the matrix element of the coordinate can be estimated in analogy with (4.2) as follows:

$$r \sim \frac{a}{R} R = a, \quad (5.1)$$

which is three orders of magnitude larger than λ_0 . The theory predicts sharp angle diagrams for the resonance, similar to those shown in Fig. 3.

Unfortunately, it was impossible to observe spin resonance with acceptors in free crystals, probably owing to the band broadening due to the lattice imperfection^[30]; the resonance can, however, be observed in crystals subject to deformations, which lower the symmetry and lift the fourfold degeneracy. The matrix element of the pure spin transition differs

*If we regard combined resonance with local centers as a method of measuring a , then it has apparently approximately the same threshold, or a threshold one order of magnitude lower, than the Hopfield method (using the fine structure of the exciton spectrum^[31]), whereas combined resonance with band carriers should make it possible to measure appreciably smaller values of a .

in this case from that given by (5.1) by a factor $\hbar\omega_S/\Delta\epsilon$ ^[33], as can be seen from perturbation theory ($\Delta\epsilon$ -level splitting due to the deformation). Therefore

$$r \sim \frac{\hbar\omega_S}{\Delta\epsilon} a. \quad (5.2)$$

Usually $\hbar\omega_S/\Delta\epsilon \sim 0.1$, and r exceeds λ_0 by two orders of magnitude.

A theoretically much more difficult problem is the case of acceptors of large radius in Ge and Si, which was analyzed by Bir, Butikov, and Pikus^[33]. Inasmuch as ideal crystals of this type have an inversion center, and the center is missing only in the local group of the impurity atom replacing one of the atoms of the main substance, the detailed variation of the potential within the confines of the cell becomes important, and the solution of the problem within the framework of the effective-mass method is impossible; only the question of an order-of-magnitude estimate can be raised here.

Being unable to present here the analysis given in^[33], we confine ourselves to crude estimates, analogous to those made above for the other cases. Inasmuch as the local group of the impurity atom is a tetrahedral group, the antisymmetrical part of the impurity-center potential can be regarded at distances exceeding a as the potential of an octupole with moment $\sim ea^3$; at distances of the order R , the perturbing potential can be estimated at

$$\frac{e^2 a^3}{\epsilon R^4} \sim E_i \left(\frac{a}{R}\right)^3.$$

Therefore, it leads to a transition matrix element

$$r \sim \left(\frac{a}{R}\right)^3 R = \left(\frac{a}{R}\right)^2 a, \quad (5.3)$$

and here $r \ll a$. At the same time, for Ge, and especially for Si, the value of r estimated in this manner exceeds λ_0 . We note, however, that according to the results of^[33], while r has a structure analogous to (5.3), it is numerically smaller; in particular, according to^[33] $r \sim \lambda_0$ for Si and $r \ll \lambda_0$ for Ge. The deformation of the sample ensuring the narrowing of the spin wave, as already noted, decreases r/λ_0 .

It is interesting to note in this connection that in accordance with the deductions of^[33], where a thorough investigation was made of different mechanisms of band broadening, in the structurally most perfect samples producible at the present time, the bandwidth should be sufficiently small also in the absence of external deformation. It is consequently of interest to undertake combined-resonance experiments in such crystals.

We have paid principal attention above to an estimate of the intensity of combined resonance; the reason for it is that combined resonance has not yet been observed experimentally on large-radius centers, so that an estimate of its intensity is essential for the

choice of a suitable direction in the experimental research; at the same time, the magnitude of the intensity of resonance is important also for an estimate of the possibility and advisability of its practical application in what follows. Once resonance is observed, the main interest should lie in the investigation of its numerous singularities.

Let us dwell in conclusion on an interesting group of investigations, which has already led to success in the experimental study of combined resonance. Bloembergen (report at the National Academy of Sciences, Washington, April, 1961^[34]) has pointed out that if the paramagnetic ions that produce small-radius impurity centers in a crystal occupy positions without an inversion center, it becomes possible to produce electric-dipole excitation of spin transitions, i.e., combined resonance; under the same conditions, in a constant external electric field E , the frequency of the spin resonance depends linearly on E (in the presence of an inversion center, only a quadratic effect will be produced).

These effects were soon observed experimentally on transition-metal ions in Si, which is a convenient and well-investigated research object: a frequency shift in a constant field was observed by Ludwig and Woodbury^[35], and combined resonance by Ludwig and Ham^[36].

The theory of these effects was developed by Ham^[37] in terms of atomic functions perturbed by the crystalline field, on the basis of the energy scheme for the interstitial ions of transition metals in silicon, proposed earlier in^[38]. He obtained by perturbation theory a spin Hamiltonian for several typical cases;* from the structure of the coefficients one can see the factors that determine the electric-dipole moment. The dipole moment is maximal when the ground state of the impurity ion is an orbital triplet ($L = 1$), for in this basis the matrix elements of the coordinate differ from zero in the local group of the impurity atom T_d . If furthermore the lowest level (resulting from the spin-orbit splitting) corresponds to $J > 1/2$, then the electric-dipole terms arise in zeroth order in H . These conditions are satisfied for the ion Mn^{2+} ($S = 2$, $L = 1$; lowest level $J = 1$), for which the electric-dipole effects are most clearly pronounced (compared with the five other investigated ions); if we write for Mn^{2+} the electric-dipole term of the spin Hamiltonian in the form

$$e r E (J_x J_z + J_z J_x),$$

where J_α are the matrices of the angular momentum and E is oriented along Oy , then in accordance with^[36] $r \approx 3 \times 10^{-10}$ cm. It is obvious that the upper boundary of the possible values of r is set for objects of this type by the ion dimension a_0 ; the actual

*On the basis of the general symmetry properties, Roĭtsin^[39] constructed and investigated the spin Hamiltonian for many other cases.

values of r , however, will always be appreciably smaller than a_0 , owing to the relative smallness of the crystalline splitting of the terms compared with the distance between the atomic terms, and for orbital singlets also because of the smallness of the spin-orbit and Zeeman splittings compared with the crystalline splittings, etc. Therefore, in the series consisting of band carriers—large-radius centers—small-radius centers, the last group of objects corresponds, as a rule, to the smallest combined-resonance intensity; nonetheless, their experimental investigation is apparently easiest.

If the impurity ion is located within the sample volume, then the crystalline field near the center has no inversion center only in certain lattice types; at the same time, the field near ions located on the surface never has an inversion center. It was therefore suggested^[39] to use the electric-dipole effect to separate the spin transitions in impurity ions near the surface.

The existence of electric-dipole spin transitions, in accordance with the dispersion relations, leads to the appearance of resonant terms in the dielectric constant near the spin frequencies. Roĭtsin^[40] considered the singularities that are introduced by these terms in various effects, which are the microwave analogs of the electro- and magneto-optical phenomena, with account of the Zeeman and Stark splittings of the spin levels.

The difference in the selection rules for combined resonance and paramagnetic resonance uncovers a possibility of saturating transitions of new types and broadens the range of applicability of electron-nuclear double resonance^[36]; thus, in particular, an increased degree of orientation of the atomic nuclei becomes attainable^[41].

Note added in proof. In a recent review, Y. Yafet (Solid State Physics, Vol. 14, 1963) analyzed still another type of terms that lead to combined resonance. In the formalism of the effective-mass method, the operator of the coordinate has in the general case the form

$$x_\alpha = i \frac{\partial}{\partial k_\alpha} - X_\alpha,$$

where the X_α connected with the interband matrix elements depend both on the components \hat{k} and, owing to the presence of spin-orbit coupling, on the spin matrices; therefore, the operators X_α make an additional contribution to the combined resonance. In the general case it should be of the same order as the contribution due to the dependence of the g -factor on \hat{k} . According to Yafet's estimates, this effect is weaker in n -InSb than that considered in in^[15]. V. I. Sheka (FTT 6, 3099 (1964), Soviet Phys. Solid State 6, 2470 (1965) calculated the intensity of combined resonance in n -InSb, using the exact solution for the 8-band scheme. According to his results, under the conditions of the experiments of^[18, 19], the mechanism of^[15], which is connected with the spin-orbit divergence of the bands, apparently predominates but should become secondary in strong quantizing magnetic fields ($\hbar\omega_c \gg kT$) at temperatures that are not too low. The additional investigations made by him show that the effect he calculated is due to the mechanism of Yafet.

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