On the theory of impurity ferromagnetism in semiconductors

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It is proposed that the effects detected recently in InSb with a Te impurity are due to beats in the Shubnikov–de Haas quantum oscillations, which change when the field is reversed. The phenomena may be attributed to the presence of a narrow electron level in the conduction band due to a part of the tellurium atoms and to the appearance of ferromagnetism in a narrow concentration range when the Fermi level approaches the impurity level. A quantitative description based on a simple model is presented.

It has recently been discovered by Andrianov, Brandt, Ioon, Fistu1 and Chudinov1–4 that a number of phenomena suggestive of ferromagnetism appear when a tellurium impurity is added to InSb in a certain range of concentration. These are, first, beats in the Shubnikov–de Haas quantum oscillations and, secondly, a change in the pattern of these oscillations when the direction of the applied magnetic field is reversed. At high temperatures, paramagnetism is observed in these samples. Analogous phenomena have been observed in certain other semiconductors of the AIIIIBV type on alloying with tellurium and selenium.

We can suggest the following model to explain these phenomena5–12. We shall imagine that the impurity atom has a narrow discrete level (for simplicity of discussion—an s-level) and that the electrons at this level interact in an “exchange” manner with the conduction electrons. If this level is far from the Fermi level, it will be completely occupied or completely empty and will give no magnetism. But if it is near the Fermi level, it may turn out that it is energetically favorable to have one electron at this level, as the exchange interaction can make the total additional energy negative.

Here, however, we must make the following reservation. The conduction electrons themselves originate only on account of the tellurium impurity. In view of this, it appears at first sight that the Fermi level can never be raised above the impurity level, in which case there is no way in which a finite range of concentration for ferromagnetism could be obtained. The way out of this situation could be that the tellurium atoms in the lattice of the semiconductor occupy slightly different positions. Most of the impurity atoms are always ionized and put electrons into the conduction band, and only a small fraction of them have a level in the necessary position. In this case, the concentration of magnetic centers \( N_m = N_{m0} = N_e / q \approx 2N_e / q < N_e \) (\( c_1 \) is the total atomic concentration of impurities, \( q > 1 \)), and the Fermi level can be situated both below and above the impurity level of interest to us. Since the position of the Fermi level and, in the final analysis, the exchange interaction depend on the impurity concentration, it is clear that ferromagnetism, if it can arise at all, will be observed only in a certain range of concentrations. The polarization of the conduction-electron spins should lead to beats in the quantum oscillations.

Thus, the model proposed can, in principle, qualitatively explain the experimental facts. We shall proceed to a quantitative analysis of its properties. We take the simplest Hamiltonian:

\[
\tilde{H} = -N_m \left[ \sum_i \phi_i^* (r) \bar{H} \phi_i (r) \right] + \sum_i \epsilon \phi_i^* (r) \phi_i (r) - J \sum_i \phi_i^* (r) \phi_{i+1}^* (r) \phi_i (r) \phi_{i+1} (r),
\]

where \( \bar{H}_0 = -\hbar^2 \nabla^2 / 2m - \mu_0 \epsilon \) is the impurity level, reckoned from \( \mu_0 \psi_0 \) is the conduction-electron annihilation operator, \( \psi_{IS} \) is the annihilation operator for an electron at an impurity level at the point \( r_1 \) and \( \epsilon \) and \( \sigma \) are Pauli matrices. We have assumed for simplicity that the impurity spin is equal to \( 1/2 \) and that the electrons have a simple isotropic quadratic spectrum. Moreover, we have not introduced any extra terms that could complicate the model, such as, e.g., the Hund term \( U_{IJ} n_I n_J \) or a term corresponding to the transition of an electron from the level \( \epsilon \) to the conduction band.

We shall discuss the qualitative role of these effects later. Below we shall use the self-consistent field approximation. This means that we assume the Kondo temperature to be below the ordering temperature and, on the other hand, we are not describing the region of the phase transition completely accurately.

In the self-consistent field approximation, an “effective field”

\[
Q = J \langle \sigma \rangle,
\]

due to the conduction electrons acts on each impurity spin. Hence the mean spin of an impurity atom is equal to

\[
\langle \sigma \rangle = n_{s-(\epsilon-Q)} - n_{s+(\epsilon+Q)} - \frac{1}{2} \left( \text{th} \frac{Q+s}{2T} - \text{th} \frac{s-Q}{2T} \right).
\]

An “effective field”

\[
H = -J N_m \langle \sigma \rangle,
\]

due to the impurities acts on the electrons, where \( N_m \) is the number of magnetic centers in unit volume. Under the influence of this “field” there appears a mean electron spin

\[
\langle \sigma \rangle = 2H = 2\nu H,
\]

where \( \nu = p_m^* / 2\pi^2 h^2 \) is the density of states of the conduction electrons (with one component of the spin).

From formulas (2)–(5), we obtain an equation for \( \langle \sigma \rangle \):

\[
\langle \sigma \rangle = \nu N_m \left[ \text{th} \left( \frac{Q+s}{2T} \right) + \text{th} \left( \frac{Q-s}{2T} \right) \right].
\]

If we disregard magnetic-anisotropy forces, the direction of \( \langle \sigma \rangle \) in space can be arbitrary. We shall fix the direction and assume this quantity to be scalar. We call attention to the fact that Eq. (6) is invariant with...
and consequently, substituting this into (9), we find does not affect the absolute value of  

But from formula (7). Making use of Eq. (7') and the fact that \( f(u) = \frac{2 \sinh u}{\cosh u + \cosh x} \), we obtain

Then \( \alpha = u/\chi f(u) \) and

Substituting this into (9), we find

For \( u \) in this formula, we must substitute the value of \( f(u) \) in the first of these equations, the solution corresponds to \( x = 2a \). Eliminating \( \alpha_0 \) from these conditions, we obtain

This gives \( x_0 = 0.644 \), and \( \alpha_0 = \frac{1}{2} \sinh x_0 = 1.117 \). If \( \alpha < \alpha_0 \), the two curves \( u(x) \) merge into each other and do not reach the abscissa. This corresponds to the results of the analysis for \( x, u \rightarrow \infty \).

Now let \( \alpha > 1 \). From (18) we obtain in this case two solutions. One of these corresponds to \( x = 1/\alpha \ll 1 \), and the other to \( x \approx 4 \alpha + \ln 4 \alpha > 1 \). In the first of these cases, \( f_1 = -\frac{1}{4\alpha} \), i.e., the solution corresponds to \( \Delta \Omega < 1 \). Determining \( u \) from Eq. (17), we have

In the second case, \( f_1 = 4a (x - 1/\alpha)^{-1} > 0 \), i.e., \( \Delta \Omega > 0 \). From Eq. (7) we obtain in this case

Thus we can say that, for \( \alpha > 1 \), we have two solutions.
tions. One of these corresponds to $\Delta \Omega < 0$ in the whole range of values of $u$ from 0 to $\infty$, while the other corresponds to $\Delta \Omega > 0$ in the whole range, i.e., is not realized. For the following, it is useful to know both these branches $u(x)$ and $u_d(x)$. They start at different $x$ and increase with different slopes. With decreasing $\alpha$, the two branches approach each other and, finally, when $\alpha = \alpha_0$, they start at the same point.

We shall determine the nature of the solutions in the vicinity of this point. First, we obtain

$$f_i = \frac{1}{2a_x x_c} \left( \frac{1 \pm \frac{1}{3}}{2a_x x_c} \right) > 0,$$

i.e., both branches correspond to $\Delta \Omega > 0$. From Eq. (7), we find in this case

$$u_i = \left[ \frac{\alpha_0 x - 1/2}{\alpha_0 x - 1/2} \right]^{1/2} (x - x_c) = 4.03(x - x_c),$$

$$u_d = 4.03(x - x_c). \quad (22)$$

This means that the left branch has $du/dx < 0$ at the starting point. But since it goes over into $u = 2a_0 x$ for $x \to \infty$, this means that the curve $u_i(x)$ is S-shaped.

Consequently, an indeterminacy appears: in the region near $x_0$ three values of $u$ correspond to one value of $x$. The fact that $\Delta \Omega > 0$ at the start of this branch is connected with precisely this indeterminacy. Thus, for $\alpha = \alpha_0$, what actually occurs is a first-order phase transition to a state with finite $u$. The situation remains the same over a certain range of values of $\alpha$ close to $\alpha_0$. Obviously, the upper boundary of this region is determined from the condition $f_1 = 0$ or $\cosh x = 2$. From this and (12), we obtain $x_0 = 1.317$ and $\alpha_0 = 1.14$. The lower boundary, in accordance with the preceding discussion, is $\alpha = 1$.

Thus, we have analyzed qualitatively the behavior of the solutions of Eq. (7) and the $\Delta \Omega$ corresponding to them, and have obtained asymptotic values. The full form of the curves $u(x)$ for different $\alpha$ is depicted in Fig. 2. The right branches (the thin lines) always correspond to $\Delta \Omega > 0$. The dashed line denotes the first-order transition (for $\alpha$ in the range $1 < \alpha < \alpha_0$).

It follows from the above analysis that for $\alpha < 1$ only $u = 0$ corresponds to a minimum of the free energy so that the condition for ferromagnetism is $\alpha > 1$. According to our definition, the level $\epsilon$ is measured from $\mu$, i.e., $\epsilon = \epsilon_0 - \mu$, where $\epsilon_0$ is the absolute height of the level. Using the definition of $\alpha$, we can write the condition $\alpha > 1$ in the form

$$|\epsilon_0 - \mu| < (3N_m)^{1/2} \frac{m}{2\pi m^*},$$

where we have put $\nu = \hbar m^*/2\pi m^*$ and $p_0 = \hbar(3\pi^2 N_m)\nu^{1/2}$ ($q$ is the ratio of the total electron concentration to the concentration of magnetic centers—cf. the beginning of the article). Since it follows from the experimental data that the necessary range of concentration is relatively small, i.e., $|\epsilon_0 - \mu| \ll \epsilon_0$, we can express $N_m$ in the right-hand side using the condition

$$\epsilon_0 = \mu = N^2(m^*)^2(3N_m q)^{1/2}/2m^*.$$

Hence, we obtain the criterion

$$|\epsilon_0 - \mu| < 2(m^*)^2(3N_m q)^{1/2}/(3n^*q). \quad (23)$$

Unfortunately, because $J$ and $q$ are unknown, it is difficult to compare this with the experimental data. It is not ruled out that the quantity $J$ is not a constant but depends essentially on $\epsilon_0 - \mu$; the criterion must then be written somewhat differently. But, provided that $J$ does not decrease more rapidly than $(|\epsilon_0 - \mu|)^{2}\nu$ as $|\epsilon_0 - \mu| \to 0$ (and there are no reasons for supposing this), the criterion (23) explains the fact that the effect is observed in a narrow range of concentration.

We now find the effect of the magnetic polarization on the Shubnikov-de Haas oscillations. For electrons with different spin orientations, the limiting moments are determined from the condition

$$p^2/2m^* = \mu + H, \quad p^2/2m^* = \mu - H,$$

where $m^*$ is the effective mass. Hence, the difference in the areas of the central sections is equal to

$$S_+ - S_-= \pi(p^2 - p)^2 - 4\pi m^*H = \frac{2m^*}{v}(\sigma). \quad (24)$$

Thus, we can directly determine $\langle \sigma \rangle$ from the beats in the Shubnikov-de Haas effect. We note that, under conditions when ferromagnetism is present, $\mu = 2\omega x$ in the limit $T \to 0$, $x \to \infty$. Substituting the definitions of $u$ and $x$, we thus find $\langle \sigma \rangle = 2\nu J N_m$, and consequently,

$$S_+ - S_- = 4\pi m^*\nu. \quad (25)$$

In the necessary concentration range, $N_m$ is essentially determined from the condition $\epsilon_0 - \mu = 0$, i.e., the beat frequency, which is proportional to $S_+ - S_-$, varies with concentration only in the case when $J$ depends strongly on $\epsilon_0 - \mu$. Establishing the very existence, and then the form, of this dependence would make it possible to refine the model we are applying. Another way of determining the dependence of $J$ on $\epsilon_0 - \mu$ is to study the concentration dependence of the Curie point. In particular, in the region $J = 0$, the condition $x = 1/\alpha$ or $T_c = \nu J N_m$ is obtained, and for lower values we can always find $\alpha$ if $T_c$ is known (Fig. 1).

We can also explain qualitatively the change in the pattern of the oscillations when the sign of the magnetic field is reversed. According to the general theory of quantum oscillations of Lifshitz and Kosevich [6], in the case under consideration the oscillation effect is described essentially by the function

$$\sin \left( \frac{c S_+}{\hbar e\mathcal{H}} \pm \frac{\nu m^*}{2m} \right) + \sin \left( \frac{c S_+}{\hbar e\mathcal{H}} \mp \frac{\nu m^*}{2m} \right)$$

where the upper signs correspond to the case when the external magnetic field $\mathcal{H}$ is parallel to $\langle \sigma \rangle$ and the lower signs correspond to the opposite direction of the field, and $g$ is the spin-splitting factor (for InSb, the quantity $g \approx 50$). From this formula we obtain

$$S_+ - S_-= \nu J N_m. \quad (26)$$
We shall assume that our sample consists of domains with different signs of the magnetization, the concentration of the (+)-regions being $c_+$. We shall also assume that the magnetic field $\mathbf{H}$ is so weak that it does not alter the pattern of the domains, and is oriented parallel to the magnetization in the (+)-regions. Then we have, in the sum,
\[
c_+\cos(a+b) + (1-c_+)\cos(a-b) - \left[\cos^2(b) - (1-2c_+)\sin^2(b)\right] \cos\left[a + \arctan\left((2c_+-1)\tan b\right)\right],
\]
\[
a = c(S_+ - S_-)/2a\mathbf{H}, \quad b = \sin\omega n_{\text{m}}/m.
\]
Change of sign of the field implies the replacement $a \rightarrow -b$; the amplitude and period of the beats are not changed, but the phase changes. This is actually observed in experiment (cf.\(^1\)) and essentially constitutes the so-called "commutation effect". The large magnitude of the $g$-factor compensates the smallness of $m^2$.

It should be noted that the effect will not be observed for $c_+ = \frac{1}{2}$, i.e., if the sample as a whole is unmagnetized. Obviously, the effect possesses anisotropy and will be absent if the field $\mathbf{H}$ is perpendicular to $\langle \hat{z} \rangle$. Of course, it is possible to achieve this only for uniaxial magnetization, i.e., if there are only two opposite types of domain. In the experiment of\(^2\), the growth characteristics of the crystal resulted in the realization of precisely this situation, with the magnetization along one of the [110] directions. The commutation effect therefore disappeared for a whole plane of directions.

Finally, the effect should vanish in the case when the field is so strong that "saturation" occurs, i.e., the domain structure disappears. In the experiment, this had not occurred in fields up to 70 kOe, and this is not easy to understand\(^3\).

We now find the total magnetization. In unit volume, we have
\[
M = \mu_B \left[\frac{g_+}{2} N_+ \langle \hat{z} \rangle + \frac{g_-}{2} \langle \hat{\sigma} \rangle\right] = \mu_B \left[\frac{g_+}{2} N_+ \langle \hat{z} \rangle \right] \langle \hat{\sigma} \rangle,
\] (27)
where $\mu_B$ is the Bohr magneton, and $g_\pm$ is the gyromagnetic ratio for the impurity spin. The quantity $M$ depends on the sign of $J$. Depending on this sign, the spins of the impurity and of the conduction electrons are polarized parallel or antiparallel to each other.

In all probability, the first term in formula (27) is much greater than the second, i.e., the impurity atoms make the main contribution to the magnetism. But in this case, for $T = 0$,
\[
M = \frac{1}{2} g_\pm u N_{\text{m}}.
\] (27')
i.e., for impurity concentrations of the order of $10^{18}$ cm$^{-3}$, the saturation magnetic moment should amount to less than $10^4$ of the moment of ordinary ferromagnets. Direct observation of the ferromagnetic moment is therefore not very simple.

Up to this point we have considered the ferromagnetic regime. We now find the paramagnetic susceptibility for $T > T_c$. For this we take into account that, in the presence of a magnetic field $\mathbf{H}$, in place of $Q$ a field $Q + \frac{1}{2} g_\pm \mu_B H$ acts on the impurity, and in place of $H$ the new effective field for the conduction electrons is $H + \frac{1}{2} g_\pm \mu_B H$. These quantities, and also $\langle \hat{z} \rangle$ and $\langle \hat{\sigma} \rangle$, are assumed to be small, and we can perform an expansion in $\langle \hat{\sigma} \rangle$. The magnetic moment is expressed by the first equality of formula (27). As a result, for the paramagnetic susceptibility we obtain
\[
\chi = 2\mu_B \left[\frac{g_+}{2} + \frac{g_-}{2}\right] \left(1 + \frac{c e x}{2ax} - 1\right). \tag{28}
\]
In reality, the electrons also possess diamagnetism. Therefore, the coefficient in the first term of formula (28) changes (it can even become negative). But this term has no singularity at $T_c$ and, moreover, in all probability, $g_\pm / \sqrt{V} \gg g$, so that the impurity paramagnetism is still the dominant effect in a wide temperature range above $T_c$. Comparing with formula (18), we see that, in the region of second-order phase transitions, $\chi$ behaves like $(T - T_c)$ as $T \rightarrow T_c$. As already noted, this cannot be considered an exact result.

Thus, the model considered gives in all cases qualitative agreement with the experimental data of the paper\(^4\). As already stated, this model is the simplest. But, for the present, there is no sense in thinking about more complicated models. This must be done when the dependence of the beat period on temperature and concentration and the dependence of $T_c$ on concentration have been obtained. We shall make qualitative remarks on the consequences of taking certain additional features into account.

First of all, we can insert into the Hamiltonian a Hund term of the type
\[
U \sum_{n_+ n_-} n_+ n_- \bar{a}_n \bar{a}_n
\]
where $g_\pm = a_+ a_- a_+$. This clearly leads to a widening of the region of existence of the ferromagnetism. In particular, for $\epsilon < 0$ and $|a| \ll U$, this region will be determined by the condition $U > \mu - \epsilon > 0$, i.e., will again be restricted with respect to the concentrations. The Curie temperature will be of the same order as in the model considered.

Furthermore, we can take into account the possibility of transition of an electron from a localized level to the conduction band; this can be described by a term of the type
\[
\sum_{n_+ n_-} [\psi^+(r) a_n + a_n^+ \psi(r)]
\]
(cf.\(^3\)). This will lead to the appearance of a finite width $\Gamma = e V^2 \nu$ of the level $E_0$. This width will compete with $T$ and $\epsilon$ and, generally speaking, will lead to a reduction of the ferromagnetism. In particular, for $|a| \ll e_{\text{r}} \sim \Gamma$ the ferromagnetism should disappear. It is possible, incidentally, that allowance for other features, e.g., the effect of the spin-orbit interaction on the electron spectrum, will also be needed for an accurate quantitative description of the experimental data when these are obtained. It is evident, however, that the basic idea proposed in this paper will remain valid.

In conclusion, I take the opportunity to express my gratitude to the authors of paper\(^5\) for communicating their data to me before publication, and, especially, to S. M. Chudinov for valuable discussions.

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\(^1\)The theory proposed in the paper\(^1\) to explain the beats in the Shubnikov-de Haas oscillations in $\text{HgSe}$\(^1\), which is based on the splitting of the electron spectrum in the Kane model\(^1\), does not explain important features of the phenomena observed in\(^1\), namely, the narrowness of the concentration range, and the "commutation effect", i.e., the change in the beats on reversal of the field.

\(^2\)For example, in the Anderson model (cf.\(^1\)), $J_{\text{a}} = V^2 \nu (\epsilon + U)$, where $V$ is the matrix element of an electron transition from a localized level to the conduction band, and $U$ is the Hund constant. The quantity
$J_A$ increases as $\epsilon = \epsilon_0 - \mu \to 0$. Of course, it is not clear that this model is applicable to the present problem. There are insufficient data at the present time for a unique choice of an accurate model. For precisely this reason, we have chosen the simplest model.

A possible explanation is the pronounced anisotropy of the "exchange" interaction, hindering the reversal of the moment, and nonuniformity of the impurity concentration, impeding the motion of the domain walls.


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