VI. BAND STRUCTURE - THEORY.

ELECTRONIC QUASIPARTICLE SPECTRUM OF FERROMAGNETIC SEMICONDUCTORS

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Résumé.— Nous discutons le spectre de quasi-particule électronique d'un semiconducteur magnétique dans le cadre du modèle s-f. On passe en revue quelques cas limites calculables exactement (saturation ferromagnétique, limite atomique, centre de gravité de la bande de conduction) ainsi que des théories approchées valables dans le cas général de façon à comprendre l'influence de la température et du remplissage des bandes sur la structure de la bande de conduction. Le schéma simple, suivant lequel en dessous de T_C , la bande de conduction d'un semiconducteur ferromagnétique se sépare en deux sous-bandes polarisées du spin, est manifestement faux. Les termes de séparation de bande se trouvent être plus complexes lorsque les poids spectraux des différences sous bandes dépendent fortement de la température T et de l'occupation des bandes n . Même à $T = 0$, la polarisation de spin électronique n'est complète que dans le cas particulier d'une bande exactement demi-pleine ($n=1$) À T fixée et pour $n < 1$ la polarisation augmente avec le remplissage de bande n .

Abstract.— We discuss the electronic quasiparticle spectrum of a ferromagnetic semiconductor within the framework of the s-f model. Some exactly calculable limiting cases (ferromagnetic saturation, atomic limit, centre of gravity of the conduction band,) as well as approximate theories for the general case are reviewed in order to understand the influence of temperature and finite band filling on the conduction band structure. The simple picture that below T_C the conduction band of a ferromagnetic semiconductor is split into two spinpolarized subbands is obviously wrong. The splitting turns out to be essentially more complex, where the spectral weights ('reduced' densities of states) of the various subbands strongly depend on temperature T and band occupation n . Even at $T=0$ the electron spin polarization is complete only for the special case of the exactly half-filled band ($n=1$). For fixed T and $n < 1$ the polarization increases with increasing band filling n .

1. **Introduction.**— We discuss some theoretical aspects concerning the electronic quasiparticle spectrum of ferromagnetic semiconductors. The characteristic properties of these substances are to be ascribed to the interaction of two welldefined electronic subsystems. The first one is built up by strongly localized electrons, the spins of which are coupled according to the Hund's rule to a total spin S per lattice site. The other subsystem consists of conduction electrons with pronounced itinerant properties. Both subsystems are thought to interact via an intraatomic exchange between localized ion spin S and conduction electron spin σ . The corresponding theoretical model is known in literature as the s-f (or d-f) model (Sect. 2.).

When treating ferromagnetic semiconductors within the framework of the s-f model one has to distinguish between two completely different areas. The first relates to systems with empty conduction bands, the usual situation for undoped, i.e. stoichiometric ferromagnetic semiconductors at low tem

peratures (Sect. 3). The second case is that of partially filled conduction bands. Quasifree carriers may be created by doping with proper impurities (e.g. $\text{EuO} + x \% \text{Gd}$). It is well-known that such finite band occupations lead to dramatic changes of the physical properties of the respective ferromagnetic semiconductor (Sect. 4).

2. **s-f model.**— The s-f model is defined by the following Hamiltonian [1-4]

$$H = H_S + H_C + H_f + H_{S-f} \quad (2.1)$$

H_S is the operator of the kinetic energy of the itinerant electrons, which in the Wannier representation is to be written as

$$H_S = \sum_{ij\sigma} T_{ij} a_{i\sigma}^+ a_{j\sigma}, \quad (2.2)$$

where $a_{i\sigma}^+$ and $a_{i\sigma}$ are respectively creation- and annihilation operators for an electron with spin σ ($\sigma = \uparrow$ or $\downarrow$) at lattice site R_i . T_{ij} is the usual hopping integral. H_C describes the Coulomb interaction of the band electrons :

$$H_C = \sum_{ijkl} v(i\sigma, j\sigma'; k\sigma', l\sigma) a_{i\sigma}^+ a_{j\sigma'}^+ a_{k\sigma'} a_{l\sigma} \quad (2.3)$$

$V(i\sigma, j\sigma'; k\sigma', l\sigma)$ is the Coulomb matrix element in the Wannier representation.- The operator H_f is devoted to the partial system of strongly localized f-electrons, the spins of which are Hund-coupled to define the spin operator S_{i1} acting on lattice site R_{i1} :

$$H_f = \sum_{i,j} J_{ij} S_{i1} \cdot S_{j1} \quad (2.4)$$

The most important term in the total Hamiltonian (2.1) is the s-f interaction operator H_{sf} which couples the two subsystems (2.2) and (2.4) by an intraatomic exchange interaction,

$$H_{sf} = -g \sum_i (S_i \cdot S_{i1})_{\sigma\sigma'} a_{i\sigma}^+ a_{i\sigma'}, \quad (2.5)$$

where S_i and S_{i1} are respectively the spin operators of the conduction electron and the magnetic moment localized at R_{i1} . g is the corresponding s-f coupling constant.

The full many body problem arising with (2.1) is not exactly solvable. Exact statements are known only for some special cases /1,5-7/ which we discuss in Sect. 3.1, in order to use them later as criteria for approximate theories.

3. Empty conduction band.- The basic requirement of this section shall be that the conduction band contains only one electron ("test electron") so that the operator H_c in (2.1) becomes meaningless.

3.1 Exactly solvable limiting cases.- Let us start with some exactly calculable limiting cases which can test the unavoidable, approximate procedures of the general case.

3.1.1 Centre of gravity of the conduction band.- The centre of gravity T_σ of the conduction band, which is defined as

$$T_\sigma = \int_{-\infty}^{+\infty} d\omega \cdot \omega \cdot \rho_\sigma(\omega) \quad (\sigma = \uparrow, \downarrow), \quad (3.1.1)$$

can be determined for both spin directions without knowing all details about the density of states $\rho_\sigma(\omega)$ of the interacting system. To show this we introduce the one-electron spectral density $A_{k\sigma}(\omega)$ /8,9/ :

$$A_{k\sigma}(\omega) = \frac{1}{N} \sum_{i,j} e^{ik(R_{i1} - R_{j1})} \frac{1}{2\pi} \int_{-\infty}^{+\infty} d(t-t') e^{i\omega(t-t')} \langle [a_{i\sigma}(t), a_{j\sigma}^+(t')] \rangle_+ \quad (3.1.2)$$

which is connected with $\rho_\sigma(\omega)$ in the following simple manner :

$$\rho_\sigma(\omega) = \frac{1}{N} \sum_k A_{k\sigma}(\omega) \quad (3.1.3)$$

Insertion of (3.1.3) and (3.1.2) into (3.1.1) leads to

$$T_\sigma = \frac{1}{N} \sum_i \langle [a_{i\sigma}, H]_-, a_{i\sigma}^+ \rangle_+ = \quad (3.1.4)$$

$$= T_0 - \frac{1}{2} g z_\sigma \langle S^z \rangle; \quad z_\sigma = \begin{cases} +1 & \text{if } \sigma = \uparrow \\ -1 & \text{if } \sigma = \downarrow \end{cases}$$

$[...]_-$ and $[...]_+$ are commutator and anticommutator, respectively. $\langle \dots \rangle$ means thermodynamic average.

The exact result (3.1.4) tells us that the conduction band is split for temperatures $T < T_C$, where the centres of gravity $T_\uparrow$ and $T_\downarrow$ of $\uparrow$ - and $\downarrow$ -spectrum are shifted against one another by an amount of $\Delta T = g \cdot \langle S^z \rangle$.

Note that this result has been proven up to now only for the centre of gravity and not at all for the band states.

3.1.2. Atomic limit.- The atomic limit is defined by a forbidden electron hopping :

$$T_{ij} \longrightarrow T_0 \cdot \delta_{ij}; \quad H_f \longrightarrow 2S J_0 \sum_i S_i^z \quad (3.1.5.)$$

Determination of the excitation spectrum is of course very simple /7,10/. The results, however, schematically plotted in fig.1, are quite instructive. Because of the s-f exchange interaction the original level T_0 splits into three sublevels for each electron spin direction. To avoid confusion let us agree upon the spin index $\uparrow$ or $\downarrow$, respectively, of the quasi-particle energies to define the spin of the electron before its excitation into the conduction "band". The spin after the excitation may be uncertain as can be seen by inspecting the involved initial and final states of the various electron transitions /10/:

$$E_{3\uparrow} : |\uparrow; 0\rangle \xrightarrow{+(\uparrow-e^-)} |\uparrow; \uparrow\rangle \quad (3.1.6)$$

$$E_{3\downarrow} : |\downarrow; 0\rangle \xrightarrow{+(\downarrow-e^-)} |\downarrow; \downarrow\rangle \quad (3.1.7)$$

$$E_{1,2\uparrow} : |\uparrow; 0\rangle \xrightarrow{+(\uparrow-e^-)} a_{1,2}^\uparrow (|\uparrow; \uparrow\rangle + b_{1,2}^\uparrow |\uparrow; \downarrow\rangle) \quad (3.1.8)$$

$$E_{1,2\uparrow} : |\uparrow; \sigma\rangle \xrightarrow{(+e^-)} a_{1,2}^\dagger \cdot (|\uparrow; \uparrow\rangle + b_{1,2}^\dagger \cdot |\uparrow; \downarrow\rangle) \quad (3.1.9)$$

$$a_{1,2}^\sigma = (1 + (b_{1,2}^\sigma)^2)^{-1/2}; b_{1,2}^\sigma = -g \cdot \left[\omega_\sigma \pm (g^2 + \omega_\sigma^2)^{1/2} \right]^{-1}; \omega_\sigma = z_\sigma 2S J_0 \quad (3.1.10)$$

The arrow before the semicolon symbolises the f-spin direction (for simplicity: $S = \frac{1}{2}$) the entry behind the spin of the s-electron. The excitation energy $E_{3\sigma}$ belongs to a transition where a σ -electron jumps onto a site with parallel ion spin. Spinflip cannot occur ("static" case). The energies $E_{1,2\sigma}$, however, correspond to final mixed spin states. Due to the s-f interaction (2.5) a σ -electron, entering a lattice site with antiparallel ion spin, has the possibility of spin-exchange with the localized moment ("dynamic" case). It is easy to show that there indeed exist two different "mixed spin states". - Of great importance are the temperature-dependent spectral weights $A_{i\sigma}$ (Fig. 1b) of the various energy levels $E_{i\sigma}$. They have the physical meaning of occupation probabilities, mathematically given by the residues of the poles of the one-particle Green function. We see for instance that in the ferromagnetic saturation only the $E_{3\uparrow}$ - and $E_{1,2\uparrow}$ -levels survive, while all the other excitations are forbidden because of zero weights.

Fig. 1 (a) Schematic plot of the electronic energy spectrum in the atomic limit. T_0 = atomic level for the non-interacting system.

(b) Spectral weights of the atomic limit level as functions of the magnetization $\langle S^z \rangle$ of the f-system.

3.1.3. Ferromagnetic saturation. - Further exact results are possible for the strong

coupling region ($g \gg W$, W = conduction band width) at $T = 0$ /7/. Starting point is a theorem of Lonke /11/ which states that the one-electron spectral density $A_{k\sigma}(\omega)$, defined in (3.1.2), is an n-pole function, i.e. a linear combination of n positively weighted δ -functions,

$$A_{k\sigma}(\omega) = \sum_{i=1}^n \alpha_{k\sigma}^{(i)} \cdot \delta(\omega - \epsilon_{k\sigma}^{(i)}), \quad (3.1.11)$$

if the determinant $\Delta_{k\sigma}^{(n)}$,

$$\Delta_{k\sigma}^{(n)} \equiv \begin{vmatrix} M_{k\sigma}^{(0)} & \dots & M_{k\sigma}^{(n)} \\ \vdots & & \vdots \\ M_{k\sigma}^{(n)} & \dots & M_{k\sigma}^{(2n)} \end{vmatrix} \quad (3.1.12)$$

is equal zero for order n and unequal zero for all lower orders $r = 1, \dots, n-1$. The element $M_{k\sigma}^{(r)}$ of the determinant $\Delta_{k\sigma}^{(n)}$ is the spectral moment of r-th order, for which we have two equivalent representations, namely

$$M_{k\sigma}^{(r)} = \int_{-\infty}^{+\infty} d\omega \cdot \omega^r \cdot A_{k\sigma}(\omega) \quad (3.1.13)$$

and

$$M_{k\sigma}^{(r)} = \langle [a_{k\sigma}, \hat{D}^r \cdot a_{k\sigma}^\dagger]_+ \rangle \quad (3.1.14)$$

where the operator D acts as follows:

$$\hat{D} \cdot A = [H, A]_- \quad (3.1.15)$$

If we calculate with (2.1) and (3.1.15) the first five spectral moments for $T=0$, thereby restricting ourselves because of the assumed strong coupling to at most linear terms in (W/g) , then we find /7/:

$$\Delta_{k\sigma}^{(1)} \equiv \frac{1}{4} g^2 S \cdot (1 - z_\sigma); \quad \Delta_{k\sigma}^{(2)} \equiv 0 \quad (3.1.16)$$

This means that in the strong coupling limit at $T=0$ the spectral density $A_{k\sigma}(\omega)$ represents a one-pole function for $\sigma=\uparrow$, and a two-pole function for $\sigma=\downarrow$, respectively. Using this fact in (3.1.11) and (3.1.13), one finds the following quasiparticle energies by fitting moments, exactly calculated according to (3.1.14):

$$\varepsilon_{k\uparrow}(T=0) = \varepsilon_{\sim}(k) - \frac{1}{2} gS \quad (3.1.17)$$

$$\varepsilon_{k\downarrow}^{(+)}(T=0) = \frac{1}{2}g(S+1) + \frac{2S}{2S+1}(\varepsilon(k) + J_0) + O(W/g) \quad (3.1.18)$$

$$\varepsilon_{k\downarrow}^{(-)}(T=0) = -\frac{1}{2}gS + \frac{1}{2S+1}(\varepsilon(k) + 4S^2 J_0) + O(W/g) \quad (3.1.19)$$

The $\uparrow$ -spectrum given by (3.1.17) holds for all g . The energy $\varepsilon_{k\downarrow}^{(+)}$ of the $\downarrow$ -spectrum has been derived in previous papers /1,5,6/, too, which however, overlooked the second excitation energy $\varepsilon_{k\downarrow}^{(-)}$. Eq. (3.1.18) shows that the subband corresponding to $\varepsilon_{k\downarrow}^{(+)}$ has a centre of gravity which is different from $T_{\downarrow}$ in (3.1.4). So the other subband is absolutely needed to shift the common centre of the total $\downarrow$ -spectrum in a suitable manner to fulfil (3.1.4)/7/. It should be pointed out that the exact results presented in this chapter clearly contradict the often used picture that the conduction band of a ferromagnetic semiconductor splits below T_C into two spinpolarized subbands. According to fig. 1 and eqs. (3.1.17) - (3.1.18) the splitting seems to be much more complex, and above all does not lead to a complete polarization of the conduction electron spin.

3.2 Method of spectral moments. - The method of spectral moments /8,9,12/ is not restricted to special ranges of values for the typical parameters such as temperature T , coupling constant g , and spin S , what may be considered as an advantage over most of the other approximate procedures.

For a complete description of the coupled electron (s)-magnon (f) system we need the electron-spectral density $A_{k\sigma}(\omega)$ defined in (3.1.2.), and the corresponding magnon-spectral density $B_q(\omega)$ /12/.

$$B_q(\omega) = \frac{1}{N} \sum_{i,j} e^{iq(R_i - R_j)} \cdot \frac{1}{2} \int_{-\infty}^{+\infty} d(t-t') e^{i\omega(t-t')} \langle [S_i^+(t), S_j^-(t')]_- \rangle \quad (3.2.1)$$

The not exactly calculable functions $A_{k\sigma}(\omega)$ and $B_q(\omega)$ are approximated as follows: First we use suitable physical arguments to fix their general structures. This is done in ref./12/ by picking out from the so-called Leh-

mann-representations of these functions

/8,12/ the most important terms. That leads for $A_{k\sigma}(\omega)$ to the following ansatz:

$$A_{k\sigma}^{(\omega)} = c_{k\sigma} \cdot \left[\delta(\omega - \varepsilon_{\sigma}(k)) + \frac{1}{N} \sum_{\sim} b_{\sigma}(k, q) * \delta(\omega - \varepsilon_{-\sigma}(k+q) + z_{\sigma} \cdot \hbar\omega_q) \right]; \quad (h=1) \quad (3.2.2)$$

The first term means physically an electron hopping without spin scattering. $\varepsilon_{\sigma}(k)$ are the electronic quasiparticle energies which have to be calculated. The second term describes spin-exchange processes between the conduction electron and the localized spin system. A $\uparrow$ -electron can absorb a magnon, thereby reversing its spin, while, on the other hand, a $\downarrow$ -electron can emit a magnon; $\hbar\omega_q$ is the magnon energy, which must be calculated selfconsistently by use of a corresponding ansatz for $B_q(\omega)$:

$$B_q^{(\omega)} = d_q \cdot \left[\delta(\omega - \omega_q) + \frac{1}{N} \sum_{k\sim} t(k, q) * \delta(\omega + \varepsilon_{\downarrow}(k+q) - \varepsilon_{\uparrow}(k)) \right] \quad (3.2.3)$$

The second term describes scattering processes in which a magnon is destroyed with simultaneous creation of an electron-hole pair, where spin conservation has to be guaranteed.

The at first unknown parameters in (3.2.2) and (3.2.3) are fitted to spectral moments, which belong to the corresponding spectral density. The moments of $A_{k\sigma}(\omega)$ are defined in (3.1.13) and (3.1.14), equivalent relations hold for the moments of $B_q(\omega)$ /12/.

The numerical evaluation of the presented theory has been performed in refs. /12,13/ for the case of Eu-chalcogenides (f.c.c. lattice, $S = 7/2$), especially for comparison with the experimentally observed red shift (rs) of the optical absorption edge of the electronic $4f^7-5d_{t_{2g}}$ transition /14,15/, given by:

$$rs(T) = \varepsilon_{\uparrow}^{(1)}(\langle S^z \rangle = 0) - \varepsilon_{\uparrow}^{(1)}(\langle S^z \rangle_T) \quad (3.2.4)$$

The upper index "1" refers to the lower band edge. If we follow ref. /2/ and choose for the s-f coupling $g = 0.188$ eV, then the

moment method predicts a total red shift rs ($T=0$) of 0.243 eV /12/ for EuO, in excellent agreement with the experimental value of 0.255 eV /15/, and the value of 0.245 eV from the perturbational treatment in reference /2/. -It is quite interesting that the red shifts of the various Eu-chalcogenides are so different (EuS : 0.18 eV, EuSe : 0.13 eV /15/) in spite of the fact that all these compounds have the same g, S , and the same lattice structure. Within the framework of the s-f model only the width W of the conduction band might be a distinctive property. Fig. 2 shows the dependence of rs (o) on the width W_0 of the "free" Bloch band for various coupling constants g , which are altogether chosen from that region commonly considered as realistic for Eu^{2+} .

Fig. 2 Dependence of the red shift on the band width W_0 for various s-f coupling constants g .

The measured edge shifts /15/ of respectively EuO, EuS, and EuSe are also indicated. From the $g = 0.2$ eV-curve (the best fit for g in the author's opinion /12,13/!) we can read off the following widths for the $5d_{t_{2g}}$ -conduction band: $W_0 = 2.05$ eV (EuO), $W_0 = 1.17$ eV (EuS), $W_0 = 0.92$ eV (EuSe), which is in good agreement with the experimental data /15/.

Finally we note that the results in fig. 2 indicate a lower bound for the s-f coupling constant g . Obviously, $g=0.14$ eV would be completely insufficient to explain the EuO-red shift.

Let us end this chapter with a critical remark. In principle the moment method is not restricted to a special range of values for the typical parameters of the system. Because of the ansatz (3.2.3) for $A_{k\sigma}^{(\omega)}$, however, it leads to the statement that the conduction band is split below T_c into only two subbands. According to the exact results of Sect. 3.1 this can be an acceptable approximation in the weak coupling region ($g \ll W$) only.

3.3. Multiband model. - The results for the atomic limit (Sect. 3.1.2), and especially for the ferromagnetic saturation (Sect. 3.1.3) clearly indicate that the splitting of the conduction band due to the s-f exchange is rather complicated. To get more information about the true bandstructure we now apply the approximate procedure of ref. /10/. Starting point is the (retarded) one-electron Green function /16/, the poles of which represent the one-particle excitation spectrum. - In the equation of motion of this function,

$$(\omega - \varepsilon(q)) G_{q\sigma}^{(\omega)} = \frac{1}{2\pi} - \frac{1}{2}g \left[z_{\sigma} \cdot T_{q\sigma}^{(\omega)} + F_{q\sigma}^{(\omega)} \right], \quad (3.3.1)$$

there appear on the right hand side two "higher" Green functions, the "static" spin function $T_{q\sigma}^{(\omega)}$,

$$T_{q\sigma}^{(\omega)} = \frac{1}{N} \sum_{ij} e^{iq(R_i - R_j)} \langle\langle S_i^z a_{i\sigma}^+ ; a_{j\sigma}^+ \rangle\rangle \quad (3.3.2)$$

and the spinflip function $F_{q\sigma}^{(\omega)}$,

$$F_{q\sigma}^{(\omega)} = \frac{1}{N} \sum_{ij} e^{iq(R_i - R_j)} \langle\langle S_i^- a_{i\sigma}^+ ; a_{j\sigma}^+ \rangle\rangle$$

$$a_{i\uparrow}^+ ; a_{j\uparrow}^+ \rangle\rangle \quad (3.3.3)$$

The function $F_{q\sigma}^{(\omega)}$ is especially interesting because its poles correspond to the energies of just those transitions between electron and ion.

From the atomic limit solution in Sect. 3.1.2. we know the exact structure of the above functions in the zero band width case. In this limiting case, $G_{q\sigma}$ and $T_{q\sigma}$ exhibit three poles and the spinflip-function $F_{q\sigma}$ two poles of first order. If we "turn on" the electron hopping ($T_{ij} \neq 0$), then the

sharp levels of the atomic case are smeared out to bands of finite width because of the kinetic energy of the electrons. The crucial point is however that this energy-uncertainty concerns the spatial Green functions. In the momentum space the kinetic energy of the electron is completely fixed by the wave vector $\vec{q}$. That means, if neglect of damping effects (finite quasiparticle life times!) is allowed, then $G_{\vec{q}\sigma}^{(\omega)}$ should represent a three-pole function even after "switching on" the electron hopping. The finite hopping probability cannot produce additional poles for fixed $\vec{q}$. Starting with the following structures for the three required functions,

$$G_{\vec{q}\sigma}^{(\omega)} = \sum_{i=1}^3 A_{i\sigma}(\vec{q}) \cdot [\omega - E_{i\sigma}(\vec{q})]^{-1} \quad (3.3.4)$$

$$T_{\vec{q}\sigma}^{(\omega)} = \sum_{i=1}^3 B_{i\sigma}(\vec{q}) \cdot [\omega - E_{i\sigma}(\vec{q})]^{-1} \quad (3.3.5)$$

$$F_{\vec{q}\sigma}^{(\omega)} = \sum_{i=1}^2 C_{i\sigma}(\vec{q}) \cdot [\omega - E_{i\sigma}(\vec{q})]^{-1}, \quad (3.3.6)$$

our approximation therefore consists in neglecting finite lifetimes of the quasiparticles. Note that the poles of $F_{\vec{q}\sigma}^{(\omega)}$ and $T_{\vec{q}\sigma}^{(\omega)}$ must be the same as those of $G_{\vec{q}\sigma}^{(\omega)}$ because otherwise the equation of motion (3.3.1) could not be fulfilled. - The still unknown quantities are again determined by fitting some spectral moments according to (3.1.13) defined as

$$M_{\vec{q}\sigma}^{(r)}(X) = \int_{-\infty}^{+\infty} d\omega \cdot \omega^r \cdot \left[\frac{1}{\pi} \text{Im} X_{\vec{q}\sigma}(\omega + i0^+) \right] \quad (3.3.7)$$

where X stands for one of the three functions G , T or F . The use of the moments, calculated according to (3.1.14), is however limited by the fact that they usually contain some correlation functions, which must be expressible by the above Green functions in order to do the procedure selfconsistently. No difficulties arise for $G_{\vec{q}\sigma}$ and $F_{\vec{q}\sigma}$ in their first four moments, so that with (3.3.6) and (3.3.7) $F_{\vec{q}\sigma}^{(\omega)}$ is completely determined. With $F_{\vec{q}\sigma}^{(\omega)}$, however, we already know two of the three poles $E_{i\sigma}(\vec{q})$ of $G_{\vec{q}\sigma}$. Therefore, for a complete solution four spectral moments of $G_{\vec{q}\sigma}^{(\omega)}$ are sufficient, too.

The excitation spectrum of a ferromagnetic semiconductor, derived in the described manner (more details in ref. /10/!) is plotted in figure 3 for an f.c.c.-lattice ($k = k(1,1,0)$) and for $S = \frac{1}{2}$, $J_0 = 10^{-3}$ eV, $W_0 = 1$ eV, $g = 5$ eV. We have chosen this huge coupling constant g to make the essentially features more transparent because one then avoids too large overlapping of the various quasiparticle bands. -

Fig. 3 (a) Upper and lower edges of the various quasiparticle subbands, arising from the original s-band due to the s-f interactions, versus f magnetization $\langle S^z \rangle$. Full lines, $\uparrow$ -bands; broken lines, $\downarrow$ -bands. ($g = 5$ eV, $S = 1/2$, $W_0 = 1$ eV).

(b) $\langle S^z \rangle$ dependence of the spectral weights of the various subbands. (l = lower band edge, u = upper band edge)

Let us list up the most remarkable points

(1) The conduction band splits for each electron spin direction into three quasiparticle subbands, the physical meaning of which exactly corresponds to that of the respective levels in the atomic limit (Fig. 1). The $E_{1,2\sigma}$ -subbands consist of the "mixed" states defined in (3.1.7) and (3.1.8), i.e. if an electron is excited to one of these subbands it has flipped its spin after the excitation with finite probability ("spinflip bands"). In the $E_{3\sigma}$ -bands, however, it retains the original spin ("static bands").

(2) The $E_{3\sigma}$ -band edges are strongly temperature dependent shifting almost proportional to $g \cdot \langle S^z \rangle$, but with T-independent widths. Quite the opposite behaviour is to be seen for the spinflip bands $E_{1,2\sigma}$.

(3) Of decisive importance is the temperature-(or equally $\langle S^Z \rangle$ -) dependence of the spectral weights $A_{i\sigma}(g)$ (Fig. 3b). It has been shown in ref. /17/, for instance, that the T-dependence of these spectral weights combined with the T-dependence of the energetic positions of the various subbands (Fig. 3a) can explain almost quantitatively the surprising result for the conduction electron spin polarization, which has been observed in recent field emission experiments performed with W-EuS junctions /18/.

(4) All weights are unequal zero even in the paramagnetic region ($\langle S^Z \rangle = 0$). Thus one observes the splitting into the various subbands also for $T > T_C$, but then the corresponding $\uparrow$ - and $\downarrow$ -subbands coincide and are equally weighted.

(5) There are strong shifts in weight between the various $\uparrow$ -subbands very close to ferromagnetic saturation, above all from $E_{2\uparrow}$ to $E_{3\uparrow}$. A corresponding redistribution of the density of states of the conduction band is indeed experimentally observed in absorption measurements and well understood within the framework of the multiband model /19/.

One should finally point out that the theory presented in this chapter reproduces correctly all known exactly solvable limiting cases (see Sect. 3.1). Furthermore, it receives impressive support by the mentioned experiments of refs /18,19/.

4. Finite band occupation.- In the previous sections we have discussed the temperature behaviour of an empty conduction band, the typical situation of an undoped ferromagnetic semiconductor. But it is well-known that the conduction band can be filled up to a certain extent by doping with suitable impurities (e.g. Gd^{3+} in $Eu^{2+}x^{2-}$, $x = 0$ or S). Such a gradual filling is accompanied by a dramatic change of the physical properties of these substances.- In order to reveal the combined temperature - and carrier concentration-dependence of the s-f spectrum we follow the CPA-formalism of refs /20,21/.

4.1 Atomic limit.- For mathematical simplification we neglect in this chapter the direct exchange operator H_f (2.4) of the localized moments because it is known from the experiment /15,12/ that typical magnon energies are smaller by some orders of magnitude than typical values for g and W . But it is clear that now the Coulomb interaction H_c (2.3) of band electrons must be taken into consideration.- It can easily be seen that for the atomic limit the spectral density $A_\sigma(\omega)$ (3.1.2) must be a four-pole function

$$A_\sigma(\omega) = \sum_{i=1}^4 \alpha_{i\sigma}(T,n) \delta(\omega - \epsilon_i) \quad (4.1.1)$$

where the poles ϵ_i represent all possible one-electron excitation energies ($T_0 = 0$, $H_f = 0$) :

$$\epsilon_1 = -\frac{1}{2}gS, \quad \epsilon_2 = \frac{1}{2}g(S+1), \quad \epsilon_3 = U + \frac{1}{2}gS, \quad \epsilon_4 = U - \frac{1}{2}g(S+1) \quad (4.1.2)$$

U is the intraatomic Coulomb matrix element. The (T,n) -dependent spectral weights $\alpha_{i\sigma}(T,n)$ are again determined by use of the first four spectral moments of $A_\sigma(\omega)/20$, 21/. Thereby appearing higher correlation functions as $\langle S^Z a_{\sigma 0}^+ a_{\sigma 0} \rangle$, $\langle S^Z a_{\sigma 0}^+ a_{\sigma \uparrow \uparrow} \rangle$, and $\langle a_{\sigma \uparrow \uparrow}^+ a_{\sigma \uparrow \uparrow} a_{\sigma \downarrow \uparrow}^+ a_{\sigma \downarrow \uparrow} \rangle$ can selfconsistently be expressed by $\alpha_{i\sigma}(T,n)$ and ϵ_i . We do not intend to repeat the rather lengthy calculation which is explicitly performed in reference /20/.

4.2. Alloy analogy.- To get information about the finite band width case we now transform the general s-f problem into the following "alloy-picture". A propagating electron will meet at a certain lattice place the atomic level ϵ_i with the probability $\alpha_{i\sigma}(T,n)$ ($i=1, \dots, 4$), according to the physical meaning of the spectral weights. That is physically the same situation as for an electron which is hopping from site to site in an alloy, consisting of four components statistically distributed over the lattice with "concentrations" $\alpha_{i\sigma}(T,n)$. For this reason we can transfer the wellknown CPA-formalism /22,23/ onto the s-f model. Starting with the frequently used semiel-

liptic density of states ρ_0 for the "free" system ($g=0$, $U=0$),

$$\rho_0(\omega) = \begin{cases} \frac{1}{\pi \cdot \eta} \left[1 - \left(\frac{\omega}{2\eta} \right)^2 \right]^{1/2} & \text{if } |\omega| \leq 2\eta \\ 0 & \text{if } |\omega| > 2\eta \end{cases} \quad (4.2.1)$$

($\eta = \frac{1}{4}W_0$), we have to solve the following CPA-equation for the Green function $G_\sigma(\omega)$ (see e.g. eq. (4.11) in ref. /22/).

$$\sum_{j=1}^4 \alpha_{j\sigma}(T, n) \frac{1 + \eta^2 G_\sigma^2(\omega) - (\omega - \epsilon_j) G_\sigma(\omega)}{\omega - \epsilon_j - \eta^2 \cdot G_\sigma(\omega)} = 0 \quad (4.2.2)$$

The solution of this equation leads immediately to the density of states $\rho_\sigma(\omega)$ of the interacting s-f system :

$$\rho_\sigma(\omega) = -\frac{1}{\pi} \text{Im } G_\sigma(\omega + i0^+) \quad (4.2.3)$$

4.3 Band structure. In figure 4 the carrier concentration dependence of $\rho_\sigma(\omega)$ is displayed for the temperature $T = 0.8 T_C$.

Fig. 4 The quasiparticle density of states of the s-f model for different conduction electron concentrations n at $T = 0.8 T_C$. Parameters are chosen appropriate for EuO : $S = 7/2$, $W = 2.05\text{eV}$, $g = 0.2\text{eV}$, $U = 2\text{eV}$, $T_C = 69.33\text{K}$.

Parameters are chosen to be appropriate to EuO (see Sect. 3.2 or refs. /12,15/): $S = 7/2$, $W_0 = 2.05\text{eV}$, $g = 0.2\text{eV}$, $T_C = 69.33\text{K}$, $U = 2\text{eV}$. The conduction band is split into several quasiparticle subbands, in a completely analogous manner to the predictions of the multiband model of Sect. 3.3 for empty bands. If we take into account that the neglect of the operator H_F leads to a contraction of the $E_{2\sigma^-}$ and $E_{3\sigma^-}$ subbands (Fig. 3), then we see that the $n=0$ -case in figure 4 clearly supports the results drawn from the multiband picture presented in sect. 3.2. - It is an interesting fact that there never appear more than three subbands per electron spin direction σ for all (T, n) -values. That means that always at least one spectral weight is zero.

Let us discuss the influence of the finite band occupation n for a special aspect, namely the conduction electron spin polarization. The spin index σ of the density of states $\rho_\sigma(\omega)$ denotes the spin of the electron before its excitation into the conduction band, so that the actual spin polarization of the partially filled band needs the following special treatment. The high energy part of the total spectrum, which we shall call $\rho_\sigma^{(c)}(\omega)$, comes into consideration only if the intra-atomic Coulomb interaction between two charge carriers is likely to take place. That is for instance the reason why for $n=0$ the upper part $\rho_\sigma^{(c)}(\omega)$ of the spectrum disappears. In this case a σ -electron cannot find a $(-\sigma)$ -electron in order to be excited into the high energy part of the σ -spectrum. If we define

$$F_\sigma(T, n) = \int d\omega \rho_\sigma^{(c)}(\omega) \quad (4.3.1)$$

then the total number N_σ of σ -electrons must be proportional to $F_{-\sigma}(T, n)$, and the electron spinpolarization is given by :

$$p(T, n) = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow} = \frac{F_\downarrow(T, n) - F_\uparrow(T, n)}{F_\downarrow(T, n) + F_\uparrow(T, n)} \quad (4.3.2)$$

The result is plotted in figure 5 for the case of doped ferromagnetic EuO. Most striking is that even for $T=0$ the conduction electrons are not fully polarized (curve A) except for the half-filled band ($n=1$). The

depolarization decreases with increasing band filling and becomes less remarkable with increasing temperature (curves B and C in Fig. 5). The results are compared in reference /21/ to photoemission data /24/ showing excellent agreement.

5. Concluding remarks.— We have discussed the influence of temperature T and carrier concentration n on the structure of the conduction band of a ferromagnetic semiconductor. As a main result we found a complex splitting of the band into several quasi-particle subbands due to the exchange interaction between itinerant electrons and localized moments.

Fig. 5 Spin polarization P as a function of temperature T/T_c and band occupation n . Parameters as in Fig. 4. Projected curves show the P - n dependence for $T/T_c = 0$ (A), 0.7 (B), 0.95 (C).

This complex band structure has been shown by some exactly solved limiting cases of the s - f model as well as by approximate theories for the general case. Experiments which support the presented results are available. On the other hand, the often used picture that the conduction band splits below T_c into two spinpolarized subbands—a picture, which can be traced back to first order perturbation theory /2/,—is obviously misleading. The conduction electron spin-

polarization shows a strong T - and n -dependence and is complete only in the special ($n=1$, $T=0$).

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