Quasiparticle band structure of ferromagnetic EuS

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We derive the temperature dependence of the electronic quasiparticle spectrum of the ferromagnetic semiconductor EuS. The study is based on a *d-f* exchange model, whose "free" part contains as important model parameters the Bloch energies $\epsilon_m(\mathbf{k})$. These quantities are determined by a self-consistent, spin-polarized band-structure calculation within the framework of density-functional theory, thereby incorporating all interactions which are not explicitly taken into account by the *d-f* model. This is approximately solved by a many-body procedure, which treats spin-exchange processes between localized $4f$ moments and itinerant conduction electrons with special care. The method is exact at $T=0$. We discuss in detail the temperature dependence of the quasiparticle density of states and of the quasiparticle band structure for the first five unoccupied conduction bands, which are mainly of $5d$ type.

In two preceding papers[1,2] we calculated the electronic quasiparticle spectrum of the ferromagnetic semiconductor EuO by use of a new method, which incorporates the results of a realistic self-consistent band-structure calculation based on density-functional theory (DFT) into a reliable many-body procedure. In this paper we apply this method to EuS. From a basic physical point of view the ferromagnetic semiconductors EuO and EuS are very similar.[3] Arising from the seven electrons in the half-filled $4f$ shell of the Eu^{2+} ion, the well-localized magnetic moment $\mu_{Eu}=7\ \mu_B$ makes EuO, as well as EuS, ideal model substances for the abstract Heisenberg concept of the so-called "localized magnetism." The fact, however, that single crystals as well as evaporated films can be used and their properties compared with each other gives EuS an advantage over EuO from an experimental point of view. A greater variety of experiments has therefore been carried out with EuS rather than with EuO, although in EuO the ferromagnetic interaction is even more pronounced[3] [T_c(EuS)=16.57 K; T_c(EuO)=69.33 K]. An interesting and very instructive example is the field emission experiment,[4-6] performed on W-EuS junctions, which has revealed a lot of information about the complicated quasiparticle structure of the electronic excitation spectrum of such magnetic $4f$ systems.[7] We consider it therefore worthwhile to derive the complete temperature-dependence quasiparticle band structure for EuS, too.

The general procedure is as follows. First we choose a suitable theoretical model, which explicitly takes into account all interactions being of decisive importance for the structure and temperature dependence of the electronic excitation spectrum of EuS. In the second step we fix the one-particle energies $\epsilon_m(\mathbf{k})$ by use of a self-consistent band-structure calculation (DFT), therewith including in an effective manner all those interactions which do not appear explicitly in our model Hamiltonian. In the final step we investigate, by use of a special many-body formalism, how the above-mentioned "important" interactions change the renormalized one-particle energies into temperature-dependent quasiparticle energies.

The choice of a proper theoretical model for ferromagnetic $4f$ systems like EuS is rather uniquely predetermined.[8] The main influence on the temperature dependence of characteristic properties of these materials must be ascribed to an exchange interaction between localized $4f$ electrons and itinerant conduction electrons:

$$H_{\mathrm{ex}}=\frac{1}{2N}\sum_{i,\sigma}\sum_{\mathbf{k},\mathbf{q}}\sum_{m}g_m\, e^{-i\mathbf{q}\cdot\mathbf{R}_i}(z_\sigma S_i^z c^\dagger_{\mathbf{k}m\sigma}c_{\mathbf{k}+\mathbf{q}m\sigma} + S_i^\sigma c^\dagger_{\mathbf{k}m-\sigma}c_{\mathbf{k}+\mathbf{q}m\sigma})\ . \quad (1)$$

$c^\dagger_{\mathbf{k}m\sigma}$ ($c_{\mathbf{k}m\sigma}$) is the creation (annihilation) operator of a conduction electron with wave vector $\mathbf{k}$ and spin σ ($\sigma=$spin$-$up, spin$-$down) in the mth subband. We shall show below that the lowest, not completely filled bands of EuS are mainly of $5d$ and $6s$ character. We number them by the index m. $\mathbf{S}_i=(S_i^x,S_i^y,S_i^z)$ is the localized $4f$ spin at site R_i ($S=\frac{7}{2}$):

$$S_j^\sigma=S_j^x+iz_\sigma S_j^y;\quad z_{\mathrm{spin-up}}=+1;\quad z_{\mathrm{spin-down}}=-1\ . \quad (2)$$

g_m is the d-f exchange constant between $4f$ electrons and conduction electrons of the mth subband. We neglect a possible $\mathbf{k}$ dependence of g_m and interband scattering.

TABLE I. Band-structure data (eV) for EuS.

	Ref. 11	Ref. 12	Present results
$4f$ spin−up bandwidth	0.54	0.39	0.52
$2p$ bandwidth	2.19	1.72(spin−up), 1.85(spin−down)	2.85
$4f$ spin−up $2p$ separation	0.44	1.25(spin−up)	1.17
$5d$ spin−up bandwidth (L_3 spin−up X_3 spin−up)	~7.8	~7.3	7.83
X_3 spin−up $2p$ gap	3.04	3.28(spin−up), 3.47(spin−down)	1.64
X_3 spin−up $4f$ spin−up gap	1.65	1.64	0.00

The kinetic energy of the conduction electrons reads as

$$H_c = \sum_{\mathbf{k}m\sigma} \epsilon_m(\mathbf{k}) c^{\dagger}_{\mathbf{k}m\sigma} c_{\mathbf{k}m\sigma} \ . \tag{3}$$

$\epsilon_m(\mathbf{k})$ are considered as renormalized Bloch energies constructed in a suitable one-particle basis. They should contain, at least in an averaged form, all interactions which are not covered directly by our model Hamiltonian.

The $4f$ moments of EuS are coupled via a certain kind of superexchange[3]

$$H_f = -\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \ . \tag{4}$$

The total d-f model is then defined by the Hamiltonian:

$$H = H_c + H_f + H_{\mathrm{ex}} \ . \tag{5}$$

Since EuS is a semiconductor, we consider the situation of a single electron excited into the otherwise empty conduction band. In our previous paper[1] we have shown that the corresponding many-body problem is exactly solvable for ferromagnetically saturated $4f$ systems ($T=0$). The solution for a spin-up electron is very simple,

$$E^{(T=0)}_{m\ \mathrm{spin-up}}(\mathbf{k}) = \epsilon_m(\mathbf{k}) - \tfrac{1}{2} g_m S \ , \tag{6}$$

while the spin-down spectrum has a complicated quasiparticle structure. For details the reader is referred to Ref. 1.

The simple exact result (6) is of decisive importance for our further procedure, because it expresses the fact that at $T=0$ the spin-up spectrum of the interacting system is quasi-identical with the "free" Bloch energies $\epsilon_m(\mathbf{k})$. "Free" here means without d-f exchange in-

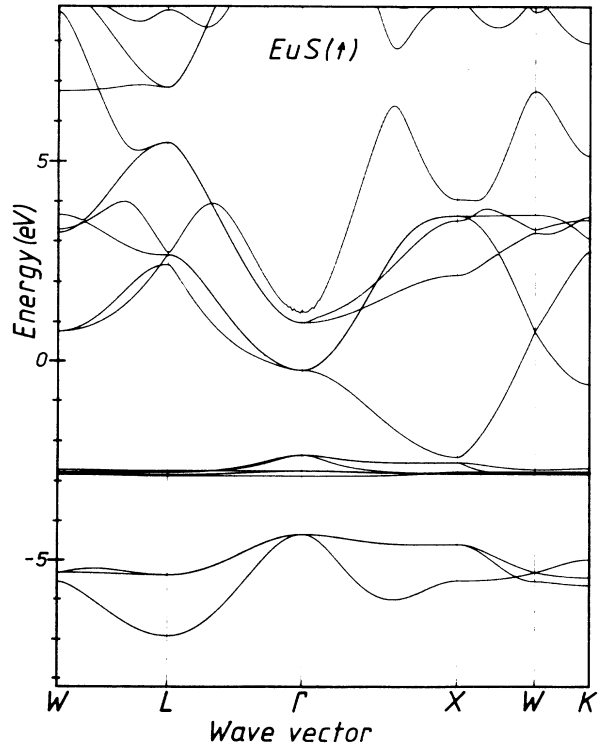

FIG. 1. Ground-state spin-up band structure of EuS as a function of wave vector, obtained from a nonrelativistic ASW calculation (Ref. 9).

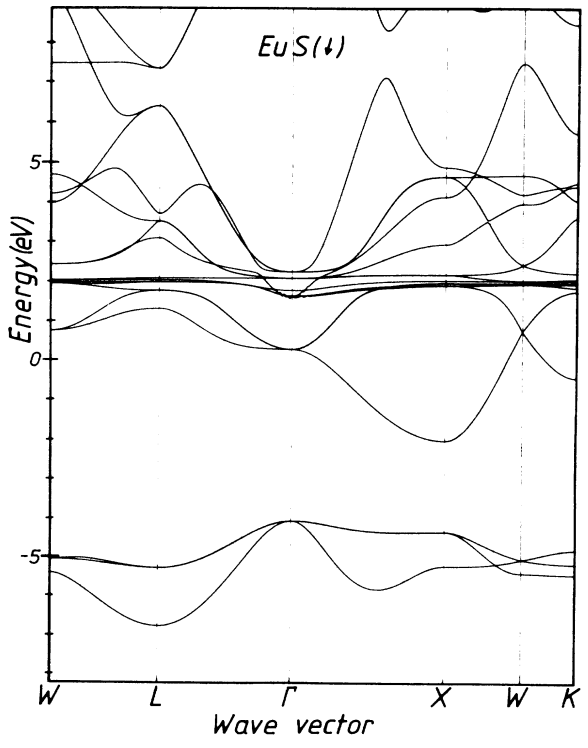

FIG. 2. The same as in Fig. 1, but for spin-down band structure.

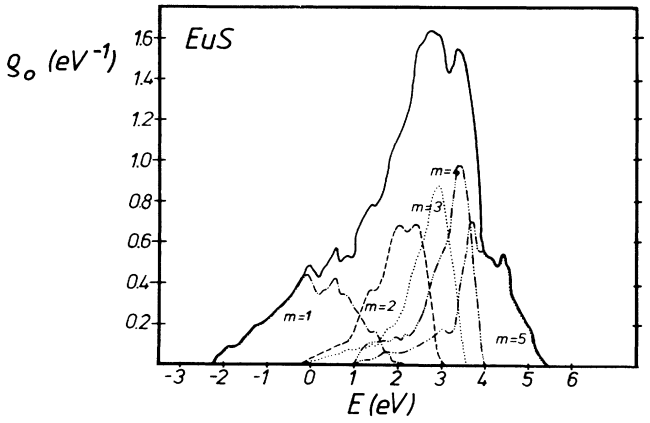

FIG. 3. Total Bloch density of states ρ_0 per atom of EuS (solid line) as a function of energy, calculated for the first five conduction bands, which are mainly of Eu^{2+}-5d character. Partial state densities ($m=1,\ldots,5$) are also indicated. The energy zero coincides with the center of gravity of the $m=1$ subband.

teraction. Performing a self-consistent, spin-polarized band-structure calculation we can identify the spin-up result with the "free" one-particle energies $\epsilon_m(\mathbf{k})$. The density-functional theory takes into account in principle *all* interactions, i.e., in a certain sense the d-f exchange, too. The latter, however, leads in the $T=0$ spin-up spectrum to a trivial additive term only, being meaningless because of the free choice of the energy zero. On the other hand, the effective single-particle energies of the density-functional theory contain all the other interaction, which are not considered explicitly within the d-f model. By this method we surely get highly realistic input parameters for our many-body treatment.

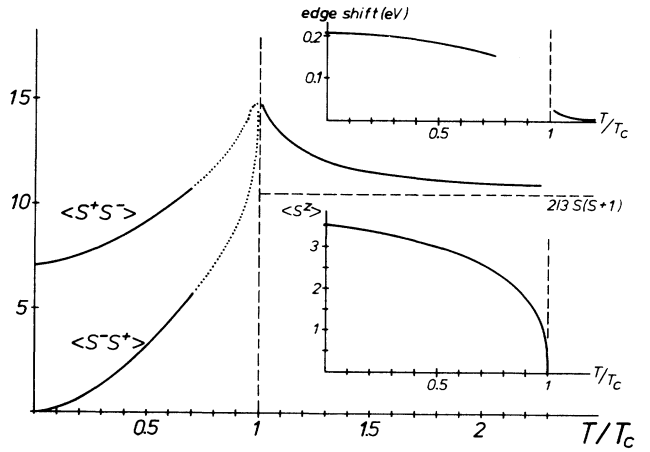

FIG. 4. Transverse intra-atomic f-spin correlation of EuS ($T_c=16.57$ K) as a function of the reduced temperature T/T_c. The low-temperature part is calculated by a moment method (Ref. 2), the high-temperature part ($T>T_c$) by a "local" mean field approximation (Ref. 12). The lower inset shows the f magnetization $\langle S^z\rangle$ as function of T/T_c according to the experimental data for EuS in Ref. 13. The upper inset shows the shift of the lower conduction band edge as a function of T/T_c following from the theory of this paper ["edge shift" (T) = edge position at $T\rightarrow\infty$ minus edge position at T].

We have performed a self-consistent nonrelativistic augmented spherical-wave (ASW) calculation[9] with the spin-polarized exchange and correlation potential V_{xc} of density-functional theory as proposed by Moruzzi *et al.*[10] Furthermore, we have used the experimental value[3] of the lattice constant of EuS $a=5.968$ Å. The resulting spin-up and spin-down bands are plotted in Figs. 1 and 2. Some relevant band-structure data are collected in Table I and compared to previous calculations. The occupied p states, stemming from the S^{2-} ion, are not interesting to us. The highly localized 4f spin-up states enter our model only as localized magnetic moments, being responsible for the magnetic properties of EuS. Since their definite energetic positions are not important for the further procedure, we need not worry about the fact that the gap between 4f spin-up states and conduction band (X_3 spin-up) is practically closed, contrary to the experiment,[3] which predicts a gap value of 1.65 eV. On the other hand, our calculated X_3 spin-up 2p gap (1.64 eV) is not as bad compared to the experimental value[3] of about 2.2 eV. Similar trends could be realized in our previous calculation on EuO.[1] Obviously, the well-known inability of the density-functional theory to predict correct gaps in insulators and semiconductors becomes worse with increasing degree of localization of the involved states. We mention that the essentially correct value of the X_3 spin-up 4f gap in Refs. 11 and 12 results from the choice of V_{xc} in those non-self-consistent nonrelativistic calculations. In fact, it has been shown in Ref. 11 that the 4f band position is extremely sensitive to the exchange-correlation potential used and may be fitted to the experimental value by varying V_{xc}. A relativistic calculation of the bands is unlikely to change this situation, and since this point does not affect our procedure we have not made efforts in this direction.

Our interest is mainly focused on the temperature dependence of the unoccupied conduction bands, particularly on the first five bands ($m=1,\ldots,5$), which are mainly Eu-5d-like. All higher lying bands shall be disregarded. The one-electron densities of states of the first

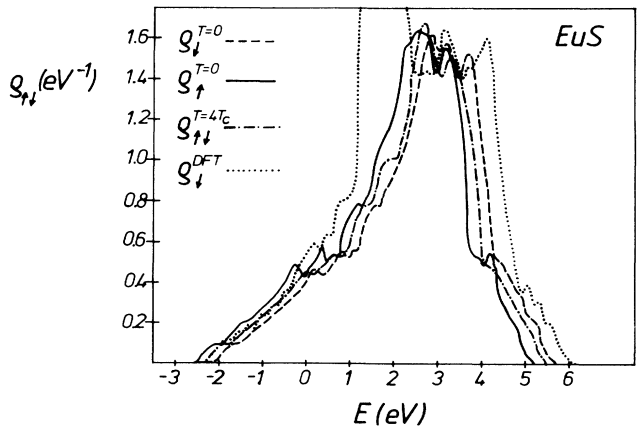

FIG. 5. Total quasiparticle density of states $\rho_{\text{spin-up spin-down}}$ per atom as a function of energy for EuS at $T=0$ and $T=4T_c$. The corresponding spin-down result of density-functional theory $\rho^{\text{DFT}}_{\text{spin-down}}$ is indicated by the dotted line.

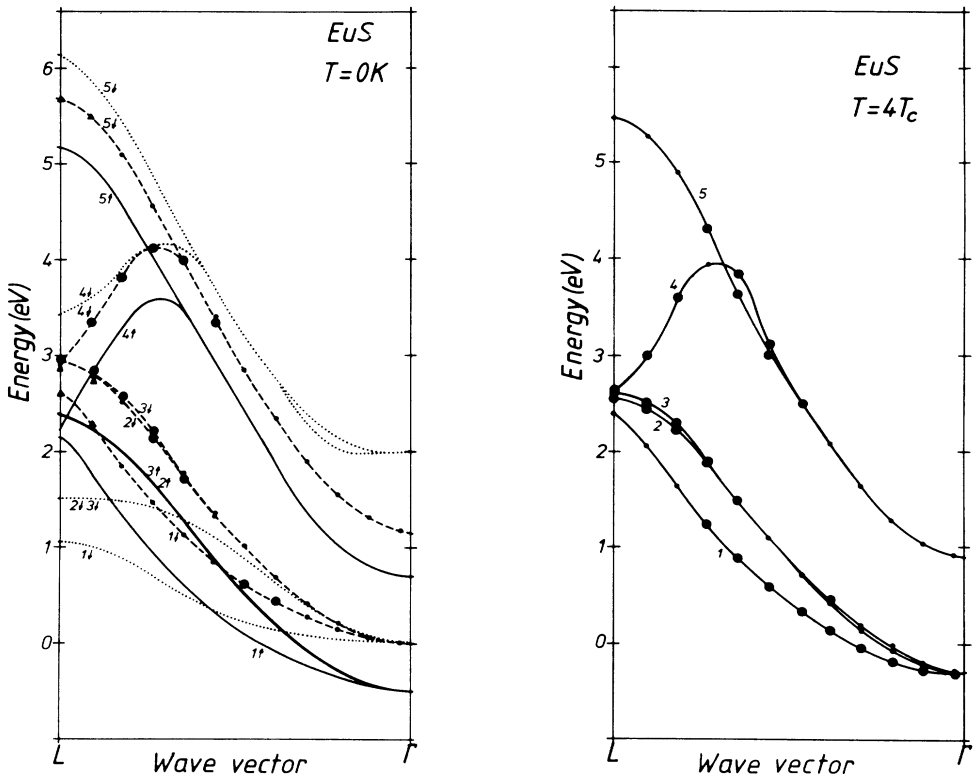

FIG. 6. Full quasiparticle band structure of EuS at $T=0$ and $T=4\ T_c$ ($T_c=16.57$ K) in the ΓL direction. Small points mark long-living quasiparticles (very sharp peaks in the spectral density), big points short-living quasiparticles (not so sharp, but still pronounced peaks in the spectral density). Triangles indicate bound states (infinitely living quasiparticles, only existent at $T=0$). In the $T=0$ case the spin-up spectrum (solid lines) consists only of bound states. Dotted lines indicate the $T=0$ spin-down result of density-functional theory.

five spin-up bands, which we need as "free" Bloch bands $\rho_0^{(m)}$ in our theoretical model, are plotted in Fig. 3.

For finite temperatures the model Hamiltonian (5) is not exactly solvable. In Ref. 2 we have proposed a many-body approach for deriving the temperature-dependent quasiparticle band structure of EuO. This approach treats the important spin-exchange processes between f moment and conduction electron with special care, and turns out to be exact for $T=0$. We shall not repeat here details of the procedure, for which the reader may be referred to our previous paper.[2] The final result for the electronic self-energy [Eq. (28) in Ref. 2] contains the f magnetization $\langle S^z\rangle$ and the f spin correlation $\langle S_i^{\sigma}S_i^{-\sigma}\rangle$. By use of a self-consistent moment method we found, for low temperatures ($0\leqq T/T_c \leqq 0.7$), the following simple relation:[2]

$$\langle S_i^{\sigma}S_i^{-\sigma}\rangle=(1+z_{\sigma})\langle S^z\rangle+(S+\langle S^z\rangle)(S-\langle S^z\rangle)\ . \quad (7)$$

In this paper we use the experimental EuS data for $\langle S^z\rangle$ as given in Ref. 13. Figure 4 shows $\langle S_i^{\sigma}S_i^{-\sigma}\rangle$ and $\langle S^z\rangle$ as functions of temperature T, where we have used in the paramagnetic region Sinkkonen's "local mean-field approximation"[14] for the correlation function.

Our model contains as an important parameter the d-f exchange constant g_m, which cannot be derived from first principles. As already done in Refs. 1 and 2 for EuO we use the red shift of the optical absorption edge for the electronic $4f^7 5d^0 \rightarrow 4f^6 5d^1$ transition, which is equivalent to a shift of the lower conduction band edge to lower energies with decreasing temperature below T_c. This red-shift effect fixes the exchange constant g_1 for the lowest subband,

$$g_1=0.145\ \text{eV}\ . \quad (8)$$

The full temperature dependence of the edge position, as it results from our theory, is exhibited as an inset in Fig. 4. The choice (8) gives a total red shift of about 0.205 eV which is slightly higher than the experimental value.[3] This has intentionally been done because density-functional theory usually gives bands which are slightly too broad (up to 10%). Smaller bandwidth, however, means less red shift (see Fig. 3 in Ref. 2). So we believe that (8) represents a realistic choice. Unfortunately, there is no similar criterion for the exchange constants of the other four $5d$ subbands. Somewhat arbitrarily we have assumed that all g_m are equal.

Figure 5 shows our results for the temperature-dependent, total quasiparticle density of states. At $T=0$ we observe an "effective" exchange splitting of about 0.5 eV, which steadily decreases with increasing temperature. Above the Curie temperature $T_c=16.57$ K[3] both spin bands of course coincide. The above-mentioned exchange splitting is, however, not at all rigid. Strictly speaking, we find that for all temperatures $T\neq 0$ both

spin spectra occupy exactly the same energy region. For $T < T_c$ the down-spin state density is, however, very much smaller at the lower edge than the up-spin state density, so that one can really speak of an "effective" exchange splitting. The comparison of $\rho^{(T=0)}_{\text{spin}-\text{down}}$ with the corresponding result $\rho^{\text{DFT}}_{\text{spin}-\text{down}}$ of the density-functional theory reveals some striking discrepancies, which are mainly due to the existence of a sharp $4f$ spin-down band in $\rho^{\text{DFT}}_{\text{spin}-\text{down}}$. We consider this $4f$ spin-down peak, however, as an artifact of density-functional theory, which predicts at $T=0$ an exchange splitting $4f\,\text{spin}-\text{down}$-$4f\,\text{spin}-\text{up}$ of some 5 eV. If we extrapolate this $T=0$ result to finite temperatures, we can explain nonsaturated ferromagnetism ($0 < T < 16.57$ K) or paramagnetism ($T > 16.57$ K) only by a partial or total overlap of the $4f\,\text{spin}-\text{up}$ and $4f\,\text{spin}-\text{down}$ subband. Since the Eu-$4f$ shell is only half filled, this necessarily would lead to the conclusion that EuS was a metal at finite temperatures, in contradiction to the experiment. Furthermore, it is extremely unlikely that a thermal energy of $k_B T_c \approx 10^{-3}$ eV may close an original exchange splitting of 5 eV at $T=0$.

The reason for this obvious failure of the density-functional theory lies in its "Stoner picture" of ferromagnetism, which assumes the magnetization to be proportional to the difference of $4f\,\text{spin}-\text{up}$ and $4f\,\text{spin}-\text{down}$ particle densities. For Heisenberg ferromagnets like EuS such an ansatz is completely unrealistic.

As described in detail in Ref. 2 for EuO we use the one-electron spectral density [Eq. (37) in Ref. 2] in order to derive the quasiparticle band structure. Normally, but not always, the spectral density shows a pronounced peak over the broad scattering spectrum. We identify the peak position with the quasiparticle energy, and its width as a measure of the quasiparticle lifetime. Examples for the resulting band structure at $T=0$ and $T=4T_c$ are plotted in Fig. 6, representatively for $\mathbf{k}$ vectors from the ΓL direction. We observe for $T < T_c$ a $\mathbf{k}$-dependent exchange splitting of each dispersion ($m = 1, \ldots, 5$), the temperature dependence of which is mainly determined by the f magnetization $\langle S^z \rangle$. Above T_c the transverse f-spin correlation $\langle S^\sigma S^{-\sigma} \rangle$ dominates the temperature-behavior of the quasiparticle band structure.

The calculated temperature dependence of the EuS quasiparticle band structure should be observable in an inverse photoemission experiment. To our knowledge such an experimental investigation of the empty states has not been performed up to now, so that a direct comparison of our results to experimental data is still excluded.

There are, however, some important qualitative aspects being completely confirmed by existing experiments. The inset of Fig. 4 shows the red shift of the lower conduction band edge as a function of temperature. For low temperatures it follows roughly the $4f$ magnetization $\langle S^z \rangle$, while for temperatures around and above T_c it is dominated by f-spin correlation functions (7). This exactly agrees with the experimental observation.[3,15]

The quasiparticle densities of states (Fig. 5) permit a natural interpretation of the field emission data found for W-EuS junctions.[4–6] The original idea was to construct by such junctions perfect electron spin filters. The expectation of fully spin-polarized tunnel electrons was based on the assumption of a spin-polarized splitting of the EuS conduction band below T_c. According to our results for $\rho_{\text{spin}-\text{up}}$ and $\rho_{\text{spin}-\text{down}}$ (Fig. 5) such a splitting, strictly speaking, does not happen. Both spin parts occupy for all temperatures exactly the same energy region, excluding therewith a total electron spin polarization. At the lower edge of the conduction band $\rho_{\text{spin}-\text{down}}(E)$ is, however, always substantially smaller than $\rho_{\text{spin}-\text{up}}(E)$, where the difference disappears for $T \geqq T_c$ and increases with decreasing temperature below T_c. Since the electrons, which start from the W-Fermi edge, will tunnel through the low-energy part of the EuS conduction band, there is nevertheless expected for $T < T_c$ a remarkable high electron spin polarization.

Our theory therefore predicts for $T > T_c$ a disappearing electron spin polarization and for $T < T_c$ polarization, which increases with decreasing temperature, reaching quite high values, but never the full saturation. This is exactly the experimental observation.[4–6]

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[1]W. Nolting, G. Borstel, and W. Borgiel, Phys. Rev. B **35**, 7015 (1987).

[2]W. Nolting, W. Borgiel, and G. Borstel, Phys. Rev. B **35**, 7025 (1987).

[3]P. Wachter, in *Handbook on the Physics and Chemistry of Rare Earths,* edited by K. A. Gschneidner and L. Eyring (North-Holland, Amsterdam, 1979), Vol. I, Chap. 19.

[4]N. Müller, W. Eckstein, W. Heiland, and W. Zinn, Phys. Rev. Lett. **29**, 1651 (1972).

[5]E. Kisker, G. Baum, A. H. Mahan, W. Raith, and B. Reihl, Phys. Rev. B **18**, 2256 (1978).

[6]K. Ertl, thesis Technische Universität München, 1981 (unpublished).

[7]W. Nolting and B. Reihl, J. Magn. Magn. Mater. **10**, 1 (1979).

[8]W. Nolting, Phys. Status. Solidi B **96**, 11 (1979).

[9]A. R. Williams, J. Kübler, and C. D. Gelatt, Phys. Rev. B **19**, 6094 (1979).

[10]V. L. Moruzzi, J. F. Janak, and A. R. Williams, in *Calculated Electronic Properties of Metals* (Pergamon, New York, 1978).

[11]S. J. Cho, Phys. Rev. B **1**, 4589 (1970).

[12]O. V. Farberovich and S. V. Vlasov, Phys. Status. Solidi B **105**, 755 (1981).

[13]J. Als-Nielsen, O. W. Dietrich, and L. Passell, Phys. Rev. B **14**, 4908 (1976).

[14]J. Sinkkonen, Phys. Rev. B **19**, 6407 (1979).

[15]J. Schoenes and P. Wachter, Phys. Rev. B **9**, 3097 (1974).