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Model Calculation of the Static Magnetic Susceptibility in Rare Earth Semiconducting Compounds

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Résumé. — Nous présentons un modèle pour le calcul de la susceptibilité magnétique statique dans des composés semi-conducteurs du type sulfure de samarium. Les états 5d sont traités schématiquement, ainsi que la bande d'énergie interdite, en s'inspirant d'un schéma de bandes réalistes pour SmS, tandis que nous considérons les deux configurations ioniques 4f° et 4f° dans leur multiplet fondamental : 4f° est un singulet et 4f° un état dégénéré (2J + 1) fois ; ces deux configurations se mélangent par l'hybridation V_{fd} entre états 4f et 5d. La susceptibilité magnétique statique permet de décrire la transition de valence en fonction de i) l'énergie de promotion Δ_+ d'un electron 4f vers les états 5d de conduction et ii) l'interaction U_{fd} entre le trou 4f subséquent et l'électron excité dans la bande 5d. Nous étendons le modèle précédent au cas des composés de type sulfure d'europium avec mélange des configurations ioniques 4f° et 4f°.

Abstract. — We present a model for the calculation of the static magnetic susceptibility in samarium sulphide type semiconducting compounds. The 5d states are schematically treated, as well as the forbidden gap, according to a realistic band scheme for SmS, whereas two ionic configurations 4f° and 4f° in their fundamental multiplets are considered: 4f° is a singlet and 4f° is a (2J + 1)-fold degenerate state; these two configurations are mixed through the f-d hybridization V_{fd}. The static magnetic susceptibility is able to describe the valence transition in terms of i) the promotion energy Δ_+ of a 4f electron into the 5d-conduction states and ii) the interaction U_{fd} between the 4f hole, left behind, and the corresponding electron excited into the 5d band. An extension of the present model is carried on to europium sulphide type compounds with (4f°, 4f°) configuration mixing.

1. Introduction

The physics related to the electronic structure of rare-earth elements has been the subject of various and numerous papers. For example, core photoemission spectra (3d and 4d-XPS) have

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been calculated in heavy rare-earth elements [1] and oxides [2]; especially the ionic model within negligible charge transfer effects has been used. 3d-XPS spectra have also been determined in light rare-earth systems with the help of an impurity Anderson model [3] which includes both the multiplet and charge transfer effects [4]. Let us just recall here that a breakthrough in the Anderson model resolution was obtained several years ago, when it was understood that both excited and ground states can be obtained, either in the metallic case, by an expansion over $1/N_t$, $N_t$ being the degeneracy of the 4f configuration [5, 6] or, in the filled band case, by an exact treatment of the many-electron problem [7]. Here our purpose is to use an adapted version of the Anderson Hamiltonian [8] in order to describe the valence fluctuation when a 4f electron of a middle-heavy rare earth element corresponding for example to SmS type semiconducting compounds [9] has the necessary energy to transit into the conduction bands. Especially it is quite interesting to calculate the corresponding static magnetic susceptibility and to use it to describe the “phase transition” considered.

Let us also recall that SmS compounds are well-known to undergo a phase transition from a black semiconducting phase (Sm$^{2+}$; 4f$^n$) to a golden metallic one (with intermediate valent state) under a pressure of 6.5 Kbar at 300 K. Similarly, the phase transition may also be induced by impurity substitution (see for example Refs. [10, 11] and Refs. therein). The present short paper will consider systems under alloying pressures such as SmS$_{1-x}$O$_x$ ($0 \leq x < 0.02$) or Eu$_{1-x}$Sm$_x$A (with A = S, Se, Te, …; $x < 0.08$). Following the impurity Anderson model, we will focus on a single rare-earth atom with two possible ionic configurations (4f$^5$, 4f$^6$) for Sm or (4f$^7$, 4f$^6$) for Eu, mixed together through the 5d states; furthermore, according to a previously calculated band structure [8], we keep the presence of a forbidden energy gap $E_g$ in the model band states. Our calculation of the static magnetic susceptibility in the systems considered is an extension of a similar calculation in light rare earth metallic systems [12]. A 4f optical absorption model in rare-earth semiconducting compounds has also been proposed in the same spirit several years ago [13]. One basic question remains: how important are intersite interactions between f sites compared to properties of the single fluctuating impurity itself? We refer the reader to a discussion on this point in the review paper [14], since it is well-known that, in the Anderson lattice, there is a competition between the intersite exchange interactions (which tend to stabilize an ordered ground state) and the valence fluctuations, or alternatively the Kondo effect, (which tend to destroy the magnetic order). However, for simplicity, in this paper, we have in mind dilute alloying pressure situations where the problem is assumed to be somewhat localized. It is out of the scope of the present work to consider more general phenomena.

The outline of the paper is as follows: first (Section 2) we present our Hamiltonian and its ground state, then (Section 3) we recall how to obtain an analytic expression of the zero-temperature susceptibility. In Section 4 we discuss our numerical results in terms of a few basic parameters in Sm-type compounds. Finally, before concluding in Section 6 we give an extension of the present model to Eu-based systems (Section 5).

2. Hamiltonian and Ground State

In order to describe a Sm-semiconducting compound, we use the following version of the impurity Anderson Hamiltonian:

$$ H = H_0 + H_{fd} $$  \hspace{1cm} (2.1)
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Fig. 1. Model density of states (DOS) represented by 2 semi-elliptic curves: \( \rho_s(\varepsilon) = \frac{\rho_s}{D_s} \sqrt{D_s^2 - (\varepsilon - \varepsilon_s)^2} \) and \( i = 1, 2 \) for the (5d) conduction and (5d) valence bands, respectively; \( \rho_s, D_s, \varepsilon_s \) are the maximum, the half-width and the centre of the \( i \) band. Mimicking the inserted d-realistic band structure [12] we take \( D_1 = 7 \) eV; \( D_2 = 1.4 \) eV; \( \varepsilon_1 = \varepsilon_c + D_1; \varepsilon_c \equiv 0; \varepsilon_2 = -D_2 - E_g + \varepsilon_c \) with \( E_g = 2 \) eV, the energy gap; \( \rho_1 \) and \( \rho_2 \) are determined in such a way that the total number of states in both bands \( N_{\text{total}} = 10 \), whereas \( N_0 = 0.1 \) in the valence band of the figure. In the inset, partial DOS are the following: \( \rho_{\text{op}} \) with a continuous curve (—); \( \rho_{\text{od}} (\Gamma_{12}) \) with a dotted curve (…) ; \( \rho_{\text{od}} (\Gamma’_{25}) \) with a dashed curve (---) and \( \rho_{\text{od}} \) with a dotted-dashed curve (—•).

with

\[
H_0 = \sum_{m,k} \varepsilon_{mk} b_{mk\sigma}^+ b_{mk\sigma} + \varepsilon_6 A_6^+ A_6 + \sum_{M=-J}^{+J} \varepsilon_5 A_M^+ A_M + \sum_{m1} \sum_{k\sigma} (V_{mk\sigma} a_{\lambda1\sigma}^+ b_{mk\sigma} + \text{h.c.}) \tag{2.2a}
\]

In \( H_0 \), the first term describes the Sm 5d-states: \( b_{mk\sigma}^+ \) creates a d-state with symmetry \( m \), momentum \( \vec{k} \) and spin \( \sigma \). Actually the 3p electrons of the anions (see [8] for SmS and refs. therein) are not explicitly taken into account in equation (2.2a), unless indirectly, through the presence of a gap in the d-bands (see inset of Fig. 1 and ref. [8]). Moreover the explicit treatment of 3p states is not essential to describe the phase transition [9]. The second and third terms of \( H_0 \) correspond to the 4f\(^6\) and 4f\(^5\) Sm configurations with respective energies \( \varepsilon_6 \) and \( \varepsilon_5 \); \( A_6^+ \) and \( A_M^+ \) label the creation operators for both configurations in their ground state multiplets \( J_6 = 0 \) and \( J_5 = J = 5/2 \). The fourth term of \( H_0 \) is the hybridization between the Sm 4f orbitals centered at site \( \lambda \) and the 5d band states. Finally the last term \( H_{\text{fd}} \) of equation (2.1) contains the Coulomb interaction between the f-hole, within the 4f\(^5\) configuration, and the electron which has been excited from 4f into the 5d states at the Sm site \( \lambda \): 

\[
H_{\text{fd}} = -\sum_{l\sigma} \sum_{m\sigma'} U_{lm} a_{\lambda l\sigma}^+ a_{\lambda m\sigma'}^+ b_{\lambda m\sigma} \equiv \sum_{Mm} U_{Mm} A_M^+ A_M^+ A_M^+ A_M^+ b_{\lambda m\sigma}^+ b_{\lambda m\sigma}
\]

with 

\[
U_{Mm} = \sum_{l\sigma} U_{lm} \phi_M |a_{l\lambda\sigma} a_{l\lambda\sigma}^+ \phi_M > |\phi_M >= A_M^+ |0 > \tag{2.2b}
\]

where \( |0 \rangle \) labels the vacuum state.

The ground state \( |\psi \rangle \) of the Hamiltonian (2.1) is built upon a linear combination of:
i) a $4f^6$-system state $|\phi_6\phi_6^0\rangle$ which includes a pure $4f^6$ configuration state $|\phi_6\rangle = A_6^+ |0\rangle$ and all the valence band (VB) states $|\phi_b^0\rangle = \sum_{m_kM\sigma} b_{m_k\sigma}^+ |0\rangle$; "<" designates the occupied states, and

ii) $|mkM\sigma \equiv b_{m_k\sigma}^+ |\Phi_M\phi_6^0\rangle$ deduced by annihilating a 4f electron and exciting it to an unoccupied 5d conduction state.

Thus we have

$$|\psi\rangle = C_6 |\phi_6\phi_b^0\rangle + \sum_{mkM\sigma} C_{mkM\sigma} |mkM\sigma\rangle$$

with

$$|C_6|^2 + \sum_{mkM\sigma} |C_{mkM\sigma}|^2 = 1.$$ 

This state $|\psi\rangle$, which is called "hybridized $4f^6$" in reference [8], was used with another state called "hybridized $4f^6$". However, when we consider the large $N_f$ limit, the hybridized $4f^6$ becomes the eigenstate of $H_0 = H - H_{\text{fd}}$. Therefore, our state $|\psi\rangle$, given by equation (2.3) is a reasonable approximate ground state of $H$ in the limit mentioned. Furthermore $U_{Mm}$ enters our equations via the small term $N_{\lambda\sigma}^0 U_{Mm}$ (see Appendix A), where $N_{\lambda\sigma}^0$ is the d-VB electron number: in the present case the order of magnitude of $\sum_{m,\sigma} N_{\lambda\sigma}^0 \approx N_d^0$ is 0.1. For simplicity, we also neglect the intersite Green functions.

Then, we have to solve the Schrödinger equation.

$$H|\psi\rangle = E|\psi\rangle$$

$$E = \varepsilon_6 + \sum_{m_k} \varepsilon_{mk} + \delta E$$

In equation (2.6) the quantity $\delta E$ is due to the configuration mixing effect and is given through a variational method by the following self-consistent equation

$$\delta E - \sum_{mkM\sigma} \frac{|V_{mkM\sigma}|^2}{\delta E - \Delta_-} + \sum_{m'\sigma'} U_{Mm'} N_{\lambda\sigma}^0 + \varepsilon_c - \varepsilon_{mk} = 0$$

with

$$\Delta_- = \varepsilon_6 + \varepsilon_c - \varepsilon_6; \quad V_{mkM\sigma} = \sum_i V_{mkli} < \phi_6 | a_{\lambda\sigma}^+ | \phi_M >$$

$\Delta_-$ means the promotion energy necessary to excite an f electron to the bottom $\varepsilon_c$ of the conduction band (CB). The coefficient $C_6$ of equation (2.3) is given by

$$|C_6|^2 \equiv W_6 = \left[ 1 + \sum_{mkM\sigma} \frac{|V_{mkM\sigma}|^2}{\delta E - \Delta_- + \sum_{m'\sigma'} U_{Mm'} N_{\lambda\sigma}^0 + \varepsilon_c - \varepsilon_{mk}} \right]^{-1}$$
$W_6$ is the weight of the $4f^6$ configuration in the whole system state $|\psi\rangle$. The corresponding valence is

$$v = 2 + W_5; \quad W_5 = 1 - W_6 \quad (2.10)$$

Within the framework of our model, the $H_{fd}$ effect is essentially a favourable renormalization effect of the promotion energy

$$\Delta_\sigma \rightarrow \tilde{\Delta}M = \Delta_\sigma - \sum_{m'm'} U_{Mm'} N_{x'm'}^0 \quad (2.11)$$

3. Static Magnetic Susceptibility

In the presence of an external magnetic field $h$ and in the case of a polarizable ground state, the energy $\delta E$ becomes $h$-dependent and equation (2.6) is then written as

$$\delta E(h) - \sum_{mkM\sigma} \left| V_{mkM\sigma} \right|^2 \frac{\delta E(h) - \tilde{\Delta}M(h) + \varepsilon_c - \varepsilon_{mk\sigma}(h)}{h} = 0 \quad (3.1)$$

Actually, when a (small) field $h$ is switched on, it removes the degeneracies of the levels and gives rise to the Zeemann terms:

$$\varepsilon_{mk\sigma}(h) = \varepsilon_{mk} - g\mu_B \sigma h \quad (3.2)$$

$$\varepsilon_{M}(h) = \varepsilon_c - gJ\mu_B Mh, \quad (3.3)$$

and extending definition (2.8):

$$\tilde{\Delta}M(h) \equiv \varepsilon_{M}(h) + \varepsilon_c - \varepsilon_6 = \tilde{\Delta}M(0) - gJ\mu_B Mh \quad (3.4)$$

where $\mu_B$ is the Bohr magneton, $g$ the spin Landé factor ($g = 2$) and $g_J$ is the Landé ratio of the considered $J$ rare-earth angular momentum

$$g_J = 1 + [J(J+1) + S(S+1) - L(L+1)]/[2J(J+1)] \quad (3.5)$$

For the ionic ground state multiplet $J = 5/2$ ($L = 5$, $S = 5/2$), we obtain $g_{5/2} = 10/35$. Following equation (3.1), the paramagnetic susceptibility can next be deduced by differentiating twice $\delta E(h)$ with respect to the field and then by taking the limit of the $h$-dependent result as $h \rightarrow 0$ [12]:

$$\chi = -\lim_{h \rightarrow 0} \frac{\partial^2 \delta E}{\partial h^2} \quad (3.6)$$

After a few manipulations, we can cast $\chi$ in the following simple but general form

$$\chi = -\frac{1}{3} \mu_J^2 \frac{\partial}{\partial \delta E} \ln(1 - W_5) \quad (3.7)$$

where

$$\mu_J = \left[ \frac{3}{4} g^2 + J(J+1)g_J^2 \right]^{1/2} \mu_B \quad (3.8)$$
Unlike the Ce-system case [12], the asymptotic expression of equation (3.7) strongly depends on the form of the density of states (DOS). For example, when the DOS is semi-elliptic, the susceptibility is proportional to \( \frac{W_5}{(1 - W_5)^2} \) and to a dimensionless coefficient \( \eta \):

\[
\chi = \frac{1}{3} \mu^2 \frac{W_5}{(1 - W_5)^2} \frac{D_1}{\pi^2} \cdot \eta \frac{\Lambda}{\Gamma^2}
\]  

(3.9)

with \( \frac{\eta}{\Gamma^2} = -\pi^2\frac{W_6^2}{D_1} \cdot \frac{\partial}{\partial \delta E} \ln(W_6) \)  

(3.10)

In equations (3.9) and (3.10), \( D_1 \) is the half CB width, whereas \( \Gamma \) has the dimension of an energy and is defined as

\[
\Gamma = N_{f}V^{2}\rho(\varepsilon_1); \quad N_{f} = 2J + 1
\]  

(3.11)

where \( \rho(\varepsilon_1) \) represents the hybridized DOS [12] at the centre of gravity \( \varepsilon_1 \) of the CB. We notice from equation (3.9) that \( \chi \) increases towards a magnetic state when \( W_5 \) tends to unity. This is for example the case for almost trivalent Sm cations in dilute SmS\(_{1-x}\)O\(_x\) alloys \((x < 0.02)\) [14]. The “magnetic” limit occurs when \( \tilde{E} = \delta E - \tilde{\Delta}M + \varepsilon_c \) tends to \( \varepsilon_c \) and consequently, \( \eta \) approaches unity. On the other hand, the singlet state \((i.e., 4f^6: J_6 = 0)\) is obtained for \( \tilde{E} \to -\infty \) corresponding to an “infinite” promotion energy \( \Delta_- \to \infty \).

Similarly, one can find the following expression which is valid for a rectangular DOS and analogous to that obtained for a Ce system [12]

\[
\chi = \frac{1}{3} \mu^2 \frac{W_5}{1 - W_5} \frac{\eta'}{\Gamma}
\]  

(3.12)

\[
\frac{\eta'}{\Gamma} = -W_6 \frac{\partial}{\partial \delta E} \ln(W_6)
\]  

(3.13)

For the numerical calculation, we only consider the general expression (3.7) with \( U_{Mm} \) independent of \( M \) and \( m \) and noted \( U_{\text{fd}} \) hereafter, so \( \tilde{\Delta}M \) of equation (2.11) is simply noted:

\[
\tilde{\Delta}_- = \Delta_- - N_{d}^{0}U_{\text{fd}}
\]  

(3.14)

4. Numerical Results

We adopt a two semi-elliptic DOS mimicking a realistic DOS in Sm semiconducting compounds [8], so that we still keep some essential characteristics (Fig. 1) of the band structure.

The behaviour of the susceptibility \( \chi \) is shown in Figure 2 with respect to \( U_{\text{fd}} \) for four values of \( V = 0.01, 0.02, 0.03, 0.04 \) eV. When \( U_{\text{fd}} \) is increased from zero to a certain value \( U_c \) depending on \( V \), \( \chi \) increases continuously from a small amount \( \chi_0 \) to an infinite value describing the transition from a “non-magnetic” to a “magnetic” state. The corresponding valence transition, i.e., transition from a mixed valent state \( v \sim 2 \) to a trivalent one, is shown in Figure 3.

Instead of varying \( U_{\text{fd}} \), it is interesting to vary \((-\Delta_-)\) to obtain a similar behaviour as in Figures 2 and 3 (Eqs. 2.9, 2.10 and 3.7). In fact, it is convenient to plot the susceptibility and the valency in terms of the renormalized promotion energy \( \tilde{\Delta}_- \). Let us notice that \( \tilde{\Delta}_- \) plays here the same role as that of \( \varepsilon_1^0 \) in the Ce system (see for example Fig. 3 of Ref. [12]). When
Fig. 2. — SmS-like susceptibility $\chi'(= \chi/\mu_B^2)$ in (eV)$^{-1}$ units versus $U_{td}$ for $\Delta_- = 0.3$ eV, $N_d^0 = 0.1$ and various values of the hybridization $V$.

Fig. 3. — Valency versus $U_{td}$ within the same parameter values as in Figure 2.

$\Delta_-$ is lowered from about $\varepsilon_c \equiv 0$ to below the p-d gap (Fig. 4) the susceptibility increases more and more, just as the Sm-valency (Fig. 5). The situation is, however, reversed for $\tilde{\Delta}_- \gg \varepsilon_c$.

From various hybridization values corresponding to Figures 2 to 5, it is clear that increasing hybridization stabilizes the "non-magnetic" singlet state relative to the "magnetic" multiplet state and appears to effectively quench the moment of the magnetically active valency. A similar tendency has already been encountered in SmS insulating compounds [8] and in light rare-earth metallic systems [12].

If we assume that $U_{td}$ behaves somewhat proportionally to an alloying pressure (as in SmS$_{1-x}$O$_x$) we recover the following experimental fact: when $x$ is increased from 0 to 0.02, the Sm cations in the vicinity of an oxygen impurity go from a singlet-valent state ($\nu \sim 2.1$) to a magnetic trivalent state [15]. For example with $V \sim 0.03$ eV and $\Delta_- = 0.3$ eV, we obtain $\nu \sim 2.07$ for $U_{td} = 0$ whereas $\nu \sim 3$ for $U_{td} \sim 13$ eV (Fig. 3).
Fig. 4. — Susceptibility $\chi'(=\chi\mu_0^2)$ in (eV)$^{-1}$ units versus $\Delta_-$ (cf. Eq. (3.14)) for $N_d=0.1$ and various values of the hybridization $V$. The scale $-2$ eV $\leq \Delta_- \leq 2$ eV corresponds to the scale $-2$ eV $\leq \Delta_- \leq 2$ eV with $U_{td}=0$ or to the scale $0$ eV $\leq \Delta_- \leq 4$ eV with $U_{td}=20$ eV.

Fig. 5. — Valency versus $\Delta_-$ within the same parameter values as in Figure 4.

5. Case of Eu Compounds

The ground state $|\psi_e>$ of Eu semiconducting compounds, in the infinite $N_f$ limit is a linear combination of two states corresponding to the two configurations: $4f^6$ and $4f^7$ which we consider in their fundamental multiplets: $J_6=0$ and $J_7=J=\frac{7}{2}$, respectively. To obtain the expression of $|\psi_e>$, we build the $4f^7$-system state from the $4f^6$-configuration by creating a d-hole, as in reference [12]:

$$|\psi_e> = B_6|\Phi_6^e\phi_b> + \sum_{\alpha\sigma} \sum_{M=-J}^{+J} B_{\alpha M\sigma}|\alpha M\sigma>,$$

$$|\alpha M\sigma> = b_{\alpha\sigma}|\Phi_M^e\phi_b>$$

(5.1)
In equation (5.1), $|\Phi_{\Phi}^{\sigma}>$ is the 4f$^{6}$ configuration state: $|\Phi_{\Phi}^{\sigma}>=A_{\Phi}^{+}|0>$, $|\Phi_{\Phi}^{\sigma}>$ is the 4f$^{7}$ configuration state: $|\Phi_{\Phi}^{\sigma}>=A_{\Phi}^{+}|0>$ and $|\phi_{b}>$ is a state including all the individual VB states $|\phi_{b}> = \prod_{\alpha\sigma} b_{\alpha\sigma}^{+}|0>$ perturbed by the Coulomb interaction between the 5d-hole and the 4f-electron (instead of the 4f hole-5d electron interaction for the Sm case):

$$H_{fd} = - \sum_{m,M,\sigma} U_{M,m} A_{M}^{+} A_{M} b_{\lambda m \sigma}^{+} b_{\lambda m \sigma}^{+}; U_{M,m} = \sum_{I \sigma} <\Phi_{M}^{\sigma}|a_{\lambda I \sigma}^{\dagger} a_{\lambda I \sigma}|\Phi_{M}^{\sigma}>$$  (5.2)

The individual state $|\alpha>$ is an eigenstate of the perturbed band Hamiltonian which we calculate from the Green function, considering $M$ and $m$ as independent:

\begin{equation}
G_{\mu}^{m}(\epsilon) \equiv \sum_{\alpha} \frac{|X_{m\mu}^{\alpha}|^2}{\epsilon - \epsilon_{\alpha} + i0^{+}} = \begin{cases} \frac{G_{\mu}^{m}(\epsilon)}{1 - U_{fd}^{m} G_{\mu}^{m}(\epsilon)} & \text{if } \mu = \lambda \\ G_{\mu}^{m}(\epsilon) & \text{otherwise} \end{cases}  
\end{equation}  (5.3)

with $X_{m\mu}^{\alpha} = <m\mu|\alpha>$; $U_{fd}^{m} \equiv U_{M,m}^{s}$, where the intersite Green functions of the unperturbed band have been neglected (for simplicity), i.e.:

$$G_{\mu \mu'}^{m m'}(\epsilon) = G_{\mu}^{m}(\epsilon) \delta_{\mu \mu'} \delta_{m m'}$$  (5.4)

Similarly to the case of Sm compounds, we can calculate the static magnetic susceptibility of Eu semiconducting compounds $\chi_{e}$:

$$\chi_{e} = - \frac{1}{3} \mu_{J}^{2} \frac{\partial}{\partial \delta E_{e}} \ln(1 - W_{J})$$  (5.5)

$\mu_{J}$ being given by equation (3.8) but for $J = J_{f}$; $W_{J}$ is the weight of the 4f$^{7}$ configuration: $W_{J} = 1 - |B_{\phi}|^2$ and $\delta E_{e}$ is the energy gain due to configuration mixing and calculated in the

---

**Fig. 6.** — Eu valency versus $(-\Delta_{e})$ (see Eq. (5.6)) and for two values of $V$. The scale 0 eV $\leq \Delta_{e} \leq 2.5$ eV corresponds to the scale 0 eV $\leq \Delta_{e} \leq 2.5$ eV for $U_{fd} = 0$ eV or to the scale $-2.5$ eV $\leq \Delta_{e} \leq 0$ eV for $U_{fd} = 0.25$ eV and $N_{d} = 0.1$. The individual state $|\alpha>$ is an eigenstate of the perturbed band Hamiltonian which we calculate from the Green function, considering $M$ and $m$ as independent:
same way as $\delta E$ for Sm compounds. We give the corresponding expressions in Appendix B. Then we study EuS-type compounds. The valence $v = 3 - W_7$ and the susceptibility $\chi$ are discussed in terms of three parameters: the hybridization $V$, the Coulomb interaction $U_\text{fd}$ and the promotion energy $\Delta_e$ necessary to promote a 4f-Eu electron to the bottom of the 5d-CB.

Let us notice from the expressions of $\delta E_e$ and $W_6^*$ (Eqs. (B-1) and (4) of Appendix B) that $\Delta_e$ and $U_\text{fd}^*$ have the same sign unlike the Sm case. The ground state solution and hence the susceptibility $\chi_e$ depend upon $\Delta_e$ and $U_\text{fd}^*$ through

$$\tilde{\Delta}_e = \Delta_e + (10 - N_d)U_\text{fd}^*$$  \hspace{1cm} (5.6)

with $N_d$ being the d-electron number $N_d \ll 10$.

If we compare the ground state solutions of Eu and Sm compounds, respectively, we note that $(-\tilde{\Delta}_e)$ corresponds to ($\tilde{\Delta}_-$). Therefore the valency and susceptibility behaviour of Eu compounds versus $(-\tilde{\Delta}_e)$ should be similar to that of Sm compounds (see Figs. 6 and 7). Increasing $\tilde{\Delta}_e$ (by increasing either $\Delta_e$ or $U_\text{fd}$) stabilizes the magnetic divalent state $4f^7$. The transition from the magnetic $4f^7$ state to the non-magnetic trivalent $4f^6$ state does not occur within the present mechanism: our calculations suggest that the considered transition in Eu compounds requires that $\tilde{\Delta}_e$ decreases and probably changes sign (by changing the sign of $\Delta_e$). However, since $(10 - N_d)U_\text{fd}^*$ is always positive, $U_\text{fd}^*$ cannot induce such a phase transition.

6. Conclusion

We developed a variational calculation based on a $\frac{1}{N_f}$ limit and an electron-hole interaction for the static magnetic susceptibility in middle heavy rare-earth (Sm, Eu) semiconducting compounds. We obtained a rather general expression of $\chi$ in terms of the magnetic configuration weight independent of the DOS form, although we can work out an analytic and asymptotic expression depending on that shape. Mimicking the semiconducting DOS by preserving a forbidden energy gap, we studied the behaviour of the susceptibility $\chi$ versus three parameters:
the promotion energy $\Delta_-$, the hybridization $V$ and the Coulomb interaction $U_{\text{fd}}$. For the determination of the susceptibility throughout the Sm valence transition, for example in the vicinity of an oxygen impurity in SmS$_{1-x}$O$_x$ alloys ($x < 0.02$), we showed [8, 9] the important role of the Coulomb interaction $U_{\text{fd}}$ effect (corresponding to the chemical pressure effect induced by alloying). More precisely, starting from nearly divalent SmS with $U_{\text{fd}} = 0$, and increasing $U_{\text{fd}}$, the susceptibility becomes, as it should finally in Sm$^{3+}$O$_{0.98}$O$_{0.02}$, more and more magnetic ($\chi$ greater and greater). Let us also mention that our susceptibility calculation can explain the experimental fact that the Sm impurities in Eu$_{1-x}$Sm$_x$O ($x < 0.08$) are trivalent, whereas the Eu cations are divalent.

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Appendix A

We briefly discuss here the validity of our state $|\psi\rangle$. Applying the Hamiltonian $H$ given by equation (2.1) on $|\psi\rangle$, we find

\[
H|\psi\rangle = E|\psi\rangle - \sum_{m\sigma} \sum_{n\sigma_1} V_{mn11}\sigma_1 a_{m\sigma}^+ a_{n\sigma_1}|\phi_0\rangle
\]

\[
- \sum_{m\sigma} \sum_{n\sigma_1} U_{m11\sigma_1} a_{m\sigma}^+ a_{n\sigma_1}|\phi_0\rangle
\]

The norm of the second state is known to go to zero in the large $N_f$ limit [6]. For the third state, its norm is of the form

\[
B = \sum_{kk'} \sum_{m\sigma} \sum_{n\sigma_1} |C_{m\sigma}|^2 U_{m1\sigma_1}^2 X_{m1\sigma_1} X_{m1\sigma_1}^2
\]

where $\sum_{kk'}$ means that the double summation is restricted to $k \neq k'$.

If we assume that $U_{m1\sigma_1} = U_{\text{fd}}$, equation (A-2) reads:

\[
B = U_{\text{fd}}^2 \frac{N_0^0}{10} (5 - \frac{N_0^0}{2}) \sum_{m\sigma} |C_{m\sigma}|^2
\]

Therefore, this term can be neglected in semiconducting compounds when $N_0^0 \ll 1$ and $U_{\text{fd}}$ is not too large.

Appendix B

The self-consistent equation for $\delta E_\sigma$ in the Eu-case is similar to that in the Sm-case, for negligible intersite Green functions.
\[
\delta E_e \equiv E_e - \sum_{\alpha \sigma} \varepsilon_\alpha + \sum_{mM\sigma} N_{\lambda m\sigma}U_{\lambda M}^m - \varepsilon_\delta = \sum_{\alpha M\sigma} \frac{|V_{\alpha M\sigma}|^2}{\delta E_e + \tilde{\Delta} M - \varepsilon_c + \varepsilon_\alpha}
\]  

(B.1)

where

\[
V_{\alpha M\sigma} = \sum_{mk} X_{\alpha}^{mk} V_{mkM\sigma}; \quad X_{\alpha}^{mk} = \langle m k | \alpha \rangle
\]

(B.2)

\[
\tilde{\Delta} M = \Delta_e + \sum_{m\sigma} (1 - N_{\lambda m\sigma}) U_{\lambda M}^m, \quad \Delta_e = \varepsilon_\delta + \varepsilon_c - \varepsilon_7
\]

(B.3)

Similarly, the 4f\(^6\) configuration weight can be expressed as follows:

\[
W_\delta^{e} \equiv |B_\delta|^2 = \left[ 1 + \sum_{\alpha M\sigma} \frac{|V_{\alpha M\sigma}|^2}{\delta E_e + \tilde{\Delta} M - \varepsilon_c + \varepsilon_\alpha} \right]^{-1}
\]

(B.4)

References