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RECENT MÖSSBAUER EFFECT STUDIES IN INTERMETALLIC AND RARE-EARTH COMPOUNDS

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Résumé. — De récentes études par Effet Mössbauer (E. M.) et par R. M. N. d'interactions hyperfines (h. f.) entre $^{151(153)}\text{Eu}$ et Eu^{2+} dans des composés EuX (X : O, S, Se, Te) et d'études d'E. M. d'interactions h. f. entre ^{166}Er et Er^{3+} dans des composés $(\text{Er}_{1-x}\text{X}_x)\text{Al}_2$ et $\text{ErNi}_{2-x}\text{Co}_x$ à structure de Laves (X : Y, Gd) révèlent dans les deux cas de remarquables transferts d'interactions h. f. Des champs h. f. intrinsèques et transférés ont été mis en évidence et quelques corrélations et dépendances entre les grandeurs magnétiques, hyperfines et la nature des liaisons ont été reconsidérées et complétées.

Abstract. — Recent Mössbauer effect (M. E.) and NMR studies of $^{151(153)}\text{Eu}/\text{Eu}^{2+}$ hyperfine (h. f.) interactions with EuX -compounds (X : O, S, Se, Te) and M. E. studies of $^{166}\text{Er}/\text{Er}^{3+}$ h. f. interactions with $(\text{Er}_{1-x}\text{X}_x)\text{Al}_2$ and $\text{ErNi}_{2-x}\text{Co}_x$ Laves-structures (X : Y, Gd) revealed significant transferred h. f. interactions in both cases. Intrinsic and transferred h. f. fields have been separated and certain systematics and correlations between magnetic, bonding, and h. f. data reconsidered and completed.

Introduction. — Among a rich variety of interesting and fundamental magnetic properties displayed by rare-earths and their compounds [1] especially two characteristic features necessitate zero applied field studies by means of microscopic tools such as nuclear resonance and neutron diffraction techniques :

1) Unusual large anisotropy energies due to large unquenched orbital moments,

2) Rather complicated spin-structures and the appearance of different ordered magnetic phases due to a competition between different indirect 4f-4f-exchange interactions.

The basic problem with nuclear resonance techniques still is to establish unambiguous relations, which can be used to deduce the effective magnetic moments of distinct atoms with zero applied field and unaffected by anisotropy and spin-structure from the measured hyperfine interaction energies.

This paper is partly a report on some recent results obtained with Eu^{2+} ions in Europium-chalcogenides using ^{151}Eu and ^{153}Eu nuclei and with intermetallic Erbium-compounds using ^{166}Er -nuclei. It is also partly a review of Mössbauer effect and n. m. r. work on these compounds.

With these examples a large body of magnetic, optical and hyperfine (h. f.) data has been accumulated in recent years. This will enable us to establish and complete certain systematics, which lead to an improved understanding of the relations used in Mössbauer effect (M. E.) studies of rare earths so far and already reviewed by Ofer [2], and Wickman [3].

I. $^{151(153)}\text{Eu}/\text{Eu}^{2+}$ hyperfine interactions in Europium-chalcogenides. — 1.1 SURVEY ON MAGNETIC AND HYPERFINE INTERACTIONS IN EuX COMPOUNDS. — First we remind of some significant relations. With S-state ions such as Eu^{2+} the h. f. field at a lattice site i is given by (1')

$$B_{1,i} = (A_{\text{core}}^s + A_{\text{ce}}^s)_i \langle S_z \rangle_i + \sum_{j \neq i} (A_{\text{ce}}^s + A_{\text{val}})_j \langle S_z \rangle_j \quad (1)$$

B_1 is mainly due to the core- and s -conduction-s-electron polarization by the atom's own spin S_i [4], but with concentrated magnetic sublattices as a rule is contributed significantly by transferred h. f. fields due to conduction and valence electron polarization by the neighbouring spins S_j . The magnitudes of the involved h. f. coupling constants are about $A_{\text{core}}^s \approx 10 \text{ T}$, A_{ce}^s and $A_{\text{val}} \approx \pm 1 \text{ T}$. At finite temperatures the average value $\langle S_z \rangle$ of the atomic spin component along the local magnetization direction z and related to the effective magnetic moment $\langle \mu \rangle = g_s \mu \langle S_z \rangle$ rather than S appears, because the spin correlation time τ_s (due to rapid thermal fluctuations of S between its eigenstates S_z ranging from $-S$ to $+S$) usually is by orders of magnitude smaller than the nuclear Larmor period $\tau_L = h/AS$ [3]. While A^s cannot be calculated for magnetic solids, precise zero field measurements of sublattice magnetizations $m(T) = M(T)/M(0)$ nevertheless are possible, if $A^s(T)/A^s(0) \approx 1$ holds or has been measured. As discussed previously [5] this proves true with EuX -compounds and enables one to deduce the data plotted in figure 1b for J_1 , J_2 , and T_c from the appropriate theoretical relations (such as $B_s(x)$, $(1 - \alpha T^{3/2})$, or $((1 - T/T_c)^\beta$, i. e. the molecular field and low temperature spin-wave approximations, or the scaling law (at $T \lesssim T_c$), respectively). Recent detailed M. E. studies of the nature of phase transitions in EuO by Groll [6] and with EuSe by Petrich [7] should be mentioned. In particular, $\beta = 0.34 \pm 0.02$ and $T_c = (69.19 \pm 0.02) \text{ K}$ has been found with EuO , while with EuSe [7] the first order phase transition suggested by Kuznia [8, 5] from a combined magnetic and n. m. r. study has been confirmed. In the following discussion only zero-temperature values of $B_1(0)$ being related to S are used.

Between ^{151}Eu nuclei in two Eu^{2+} -compounds of s -electron densities $L_1(0)$ and $L_2(0)$ the isomer shift

(1') Hyperfine fields here are given in the internationally recommended B-units « Tesla » ($1\text{T} = 10^4\text{G} = 1 \text{ Vsm}^{-2}$), which fortunately differ by only a factor of 10 from the so far utilized H-units kOe.

with respect to a certain gamma ray source (e. g. ^{151}Sm in Sm_2O_3) is given by [9]

$$\delta_{is} = (2\pi/3) Ze^2 \delta \langle r^2 \rangle (L_1(0) - L_2(0)). \quad (2)$$

(Ze nuclear charge, $\delta \langle r^2 \rangle$ difference of charge radii between the nuclear ground and excited state involved in the Mössbauer transition.) Table 1 summarizes all nuclear data useful in this discussion.

TABLE I

Nuclear Data ^(a) of the Isotopes ^{151}Eu , ^{153}Eu , and ^{166}Er

	^{151}Eu	^{153}Eu	^{166}Er
Natural Isotope Abundance : (%)	47.77	52.23	32.9
Spins I_g : (\hbar)	5/2	5/2	0
I_e : (\hbar)	7/2	7/2	2
Magn. Moments			
μ_g : (n. m.)	3.439 1	1.518 6	0
μ_e : (n. m.)	2.57	3.21	0.63
Quadrupole Moments			
Q_g : (b)	1.18 (2)	2.95 (2)	0
$(1 - R_Q) Q_e$: (b)	1.5	—	—1.6
$\mu_g/(Ih)$: (MHz/T)	10.486 1	4.630 3	—
$\delta \langle r^2 \rangle$: (fm) ²	0.028	—0.15	—
E_γ : (keV)	21.6	97.4	80.6
$(\Delta E/\Delta v)$: (10^{-6} eV/cm/s)	0.724	3.26	2.686

($\hbar = 1.0545 \times 10^{-34}$ VAs², 1(n. m.) = 5.0505×10^{-27} VAsT⁻¹
 1(b) = 10^{-24} cm², 1(fm)² = $(10^{-13}$ cm)²)

(^a) E. g. see OFER [2].

The magnetic, electric, and optical properties of the EuX magnetic semiconductors (X : O, S, Se, Te) discovered with EuO in 1961 have been extensively reviewed recently [10, 11]. Figure 1 summarizes certain optical and magnetic data also discussed previously [5], but significant for the intended discussion of correlations between the magnetic interactions J_1 and J_2 (Fig. 1b), the bonding character (ionicity j_p), and the h. f. interactions (i. e. isomer shift δ_{is} and h. f. field $B_1(0)$) (Fig. 1c).

In EuX, the magnetic Eu^{++} ions occupy either of two f. c. c. sublattices of a cubic rocksalt structure (space group $\text{Fm } 3m - \text{O}_h^5$) and exhibit a spin-only moment of nearly $7 \mu_B$ well-localized on the 4f-shell and having the groundstate $4f^7 \cdot ^8S_{7/2}$. The exchange interaction J_1 is due to the coupling of a Eu^{++} ion to its twelve next Eu-neighbours via an overlap of the Eu^{++} -5d- t_{2g} -orbitals, while J_2 is due to a superexchange to the six next nearest neighbours via the overlap of Eu^{++} -5d- e_g -orbitals with p-orbitals of the intermediate anion. J_1 is positive and tends to align the Eu^{++} -spins parallel, whereas J_2 is negative favouring an antiparallel alignment of spins in adjacent (111)-planes. The exchange interactions are related to the intra-atomic exchange A_{fd} between the 4f- and 5d-electrons and to the attributed electron transfer and interband energies b_i and U_i by relations of the form $J_i = A_{fd} b_i^2 / S_{4f} U_i^2$. These have been discussed in more detail by Goodenough [12] and with emphasis placed on the EuX-compounds by Kasuya [13] recently. Generally $(b_i/U_i)^2$ will decrease with increasing U_i

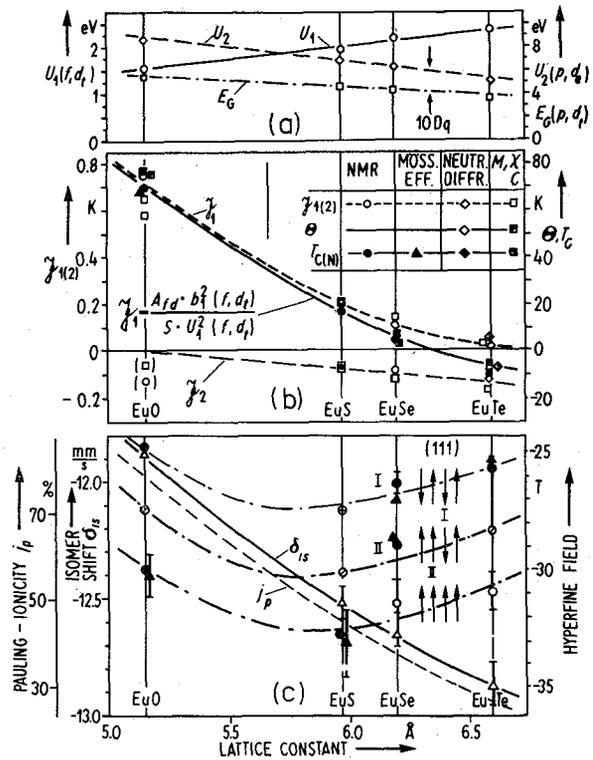


FIG. 1. — Summary of the optical results on band structure and transition energies of EuX compounds (a), the related magnetic exchange data (b), and the hyperfine interaction data (c) as obtained from n. m. r. (●) and M. E. studies (▲ h. f. fields, △ isomer shifts; ○) calculated from EuSe n. m. r. data).

and decreasing overlap integrals (included in b_i). The energies $U_1(f, d_i)$ and $U_2(p, d_e)$ necessary to transfer electrons from either 4f⁷-levels to 5d- t_{2g} -levels or from p-levels at top of the valence band into 5d- e_g -levels, respectively, have been deduced from optical absorption spectra as reviewed recently by Dimmock [14]. The dependence of U_i of the lattice constant (Fig. 1a) corresponds to that observed with J_1 and J_2 . The optical gap energy E_G , the crystal field splitting $10Dq$ between the 5d- t_{2g} -triplet and the 5d- e_g -doublet may give a feeling of the EuX-band structure. With this background on band and magnetic properties let us look for correlations with the hyperfine interactions plotted in figure 1c.

1.2 SYSTEMATICS OF $^{151,153}\text{Eu}/\text{Eu}^{2+}$ -HYPERFINE INTERACTIONS. — Several attempts have been made previously to establish correlations between δ_{is} and B_1 with Eu^{++} -compounds [15, 16]. Due to the omitted separation between intrinsic and transferred B_1 -contributions (eq. (1)) they have been partially successful only.

With Europium metal the significance and possibility of this separation have been clearly demonstrated by the recent M. E. work of Hüfner and co-workers [17, 18].

With the EuX-family the recent n. m. r. study of metamagnetic EuSe by Kuznia [8] revealed the existence and magnitude of transferred hyperfine fields. As discussed in detail in a previous paper [5], from these n. m. r. data obtained with EuSe in the ferrimagnetic phase two distinct h. f. fields

$$B^N(0) = -(29.3 \pm 0.25) \text{ T}$$

and

$$B^S(0) = -(26.2 \pm 0.25) \text{ T}$$

attributed to the sublattices N and S have been deduced. The neutron diffraction results by Fischer [19] revealed three spin structures in EuSe consisting of ferromagnetic (111)-planes with their magnetization pointing either north (N) or south (S). Following the [111]-axis one observes a NNSS-period with the anti-ferromagnetic phase, and a NNS-period with the ferrimagnetic phase in accordance with the magnetic and n. m. r. results [5, 8]. EuTe displays the MnO-spin structure NSNS [20], while for the ferromagnetic phase N is assumed. Hence, considering a central \bar{N} -spin three cases have to be distinguished with respect to the two adjacent (111)-planes, i. e. $\overline{N\bar{N}N}$, $\overline{N\bar{N}S}$, $\overline{S\bar{N}S}$ (see arrows in Fig. 1c and 2). Taking into account further that 6 n.n. are present in the central \bar{N} -plane, added by 3 n.n. and 3 n.n.n. of each adjacent (111)-plane we arrive at the result, that each configuration differs by 6 n.n. and 6 n.n.n. contributions, i. e.

$$2 \Delta B(111) = 6 \Delta B_1 + 6 \Delta B_2 = (29.3 - 26.2) \text{ T} = 3.1 \text{ T}.$$

From this result and the attributed relations and data of the observed fields (i. e.

$$B_1(\overline{N\bar{N}N}) = B_{1,i}^0 + 6 \Delta B_1 + 2 \Delta B(111) = -29.8$$

and 32.7 T [5] with EuO and EuS, respectively,

$$B_1(\overline{N\bar{N}S}) = B_{1,i}^0 + 6 B_1 = B^N(0) \text{ and}$$

$$B(\overline{N\bar{S}N}) = B_{1,i}^0 - 6 \Delta B_2 = B^S(0)$$

with EuSe, and $B_1(\overline{S\bar{N}S}) = B_{1,i}^0 - 6 \Delta B_2 = -25.5 \text{ T}$ [21] with EuTe) one obtains an estimate of the transferred fields, and of the intrinsic contributions, i. e. $B_{1,i}^0 = (A_{\text{core}}^s + A_{\text{ce}}^s)_i \langle S_i \rangle \approx B_1(\overline{S\bar{N}S})$. With these separated B_1 -contributions the B_1 vs a_0 -plot in figure 1c looks much more systematic than that revealed by the measured B_1 -data (full dots in Fig. 1c). In figure 1c also δ_{is} -data taken from an ^{151}Eu M. E. study of Eu^{2+} - and Eu^{3+} -compounds by Gerth [22] and B_1 -data (2) from recent M. E. studies are shown.

From a synopsis of figures 1a, b, and c the mutual correlations between isomer shifts, optical, and magnetic data and also those with the lattice constants are obvious. In particular, the simultaneous decrease of E_G , $10 Dq$, U_2 , and j_p accompanied by an increase of J_2 and decrease of J_1 is mutually consistent and reasonable. In addition a linear relation between δ_{is} and the Pauling ionicity [24] exists as pointed out already in [22].

However, $B_{1,i}(a_0)$, i. e. the spin density at the Eunuclous does not seem to fit in these systematics. It is also not obvious, why the s-electron density $L_s(0)$ increases (i. e. leads to more positive δ_{is}) with j , while the EuX-bonding electrons become increasingly removed from Eu and concentrated on X. Kienle and co-workers [22] suggested this to be due to an increasing

(2) Note that in EuSe the M. E. studies resolve only one h. f. field, which, however, is found either near $B^S(-26.8 \text{ T}$ [23]) or near $B^N(-28.7 \text{ T}$ [7]).

participation of 5p-electrons to the bond causing a decrease of screening with the Eu outer s-shells. However, from band structure and the B_1 -systematics to be discussed now, the Eu-5d-electrons should be related to this effect rather than the 5p-electrons.

In figure 2 the B_1 -data of M. E. and N. M. R. studies

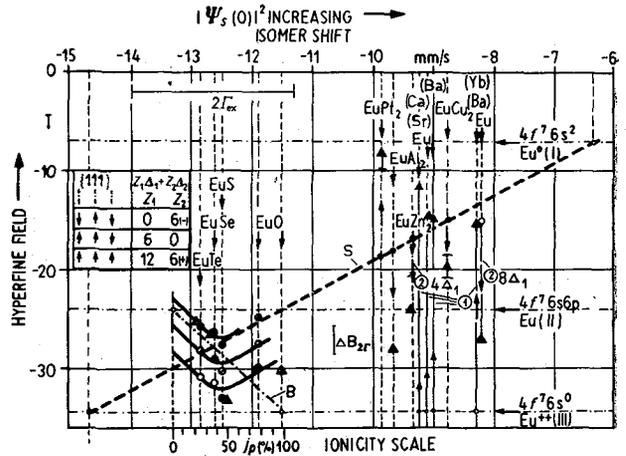


FIG. 2. — Summary of intrinsic ($B_{1,i}(4f^7 6s^0) + \textcircled{1}$) and transferred ($\textcircled{2}$) h. f. fields from $^{151}(^{153})\text{Eu}/\text{Eu}^{2+}$ -M. E. (\blacktriangle) and n. m. r. (\bullet) studies of EuX compounds, compared to results on Eu(X)- and EuX_2 -metals, and related to isomer shifts δ_{is} (i. e. s-electron densities at the Eu nuclei), nature of bonding (ionicity j_p), B_1 -values of atomic spectroscopy obtained with $4f^7 6s^6 p$ - and $4f^7 6s^2$ -Eu-configurations, and the ENDOR result with $\text{Eu}^{2+}(4f^7 6s^0)$ in CaF_2 .

Erratum : In the figure S and B are like in the text but without the circle.

are plotted against the attributed isomer shifts. Included are B_1 -data deduced by means of atomic spectroscopy [25] and Endor-techniques [26] for the Eu-configurations $(4f^7 5s^2 5p^6)6s^2$, $6s^6 p$, $6s^0$. In addition Wickman's results on EuX_2 -Laves structures [16] and Hüfner's results [17, 18] on Eu-metal diluted with Ca, Sr, Ba, and Yb are plotted. Finally the complete Pauling ionicity scale as related to $\delta_{is}(\text{EuX})$ is shown. If one extrapolates the two branches revealed by the intrinsic fields $B_{1,i}^0(\text{EuX})$ either between EuS and EuO or between EuSe and EuTe one obtains two base lines having a rather suggestive character with respect to B_1 - δ_{is} and B_1 - j_p -correlations. The one branch is labelled « S », since it is closely related to s-electron densities and isomer shifts. The second branch is labelled « B », since it is related to the bonding character and to the h. f. fields B_1 rather than to δ_{is} . « S » intersects with

$$B_{1,i}(4f^7 6s^0) = (A_{\text{core}}^s \cdot S)_i = -34.2 \text{ T}$$

at $\delta_{is} = -14.7 \text{ mm/s}$, passes Hüfner's intrinsic fields $(A_{\text{core}}^s + A_{\text{ce}}^s)_i S_i$ obtained with Eu in Sr, and Ba and intersects with $B_1(4f^7 6s^2)$ of the free atom at $\delta_{is} = -6.3 \text{ mm/s}$. The base line suggested from the bonding branch « B » intersects with $B_1(4f^7 6s 6p)$ near $j_p = 0$ and with $B_1(4f^7)$ at about $j_p = 100\%$. Hence, both branches display some reasonable features. Branch « S » related to δ_{is} , which in fact is a charge density scale, suggests $(A_{\text{ce}}^s S)_i$ of eq. (1), i. e. the s-electron polarization by the atom's own 4f-shell and

labelled ① in figure 2, to be correlated linearly with δ_{is} . In particular, the increase of this term from 0 (at $\delta_{is} = -14.7$ mm/s) to 27.2 T (at $\delta_{is} = -6.3$ mm/s) and the corresponding decrease of $B_{1,i}$ from -34.2 T to -7 T, is seen to be correlated with an increase of δ_{is} . The isomer shift between the $4f^7 6s^2$ - and $4f^7 6s^0$ -configurations deduced from the $B_{1,i}$ -line «S» is about 8 mm/s and thus differs by a factor 2 from the value 17.6 mm/s deduced from isotope shifts by Brix [9]. However, it is in fair agreement with $\Delta\delta_{is}(4f^7 6s^2 - 4f^7 6s^0) \approx 10$ mm/s obtained from a recent Hartree-Fock (HFS) calculation [27]. Hence, we hope that the base line «S» will prove to be unique⁽³⁾. Since it predicts an estimate of the transferred h. f. fields (labelled ② in Fig. 2) in EuX_2 , dilution of Eu with Yb or Sr e. g. in EuAl_2 would provide an experimental check of the proposed base line «S».

Let us next discuss the probable reasons for the change from branch «S» to branch «B» displayed with EuX compounds at EuS, but in a similar way also in Hufner's results between Eu-Ba(Sr) and Eu-Ca (see Fig. 2 and [18]). The $B_{1,i}$ -term ($A_{ce}^s S$)_{*i*} of eq. (1) is found to increase again, while δ_{is} and L_s are further decreasing. Hence, there must be an additional contribution to ① not related to the s-electron density. The apparent correlation of this branch with j_p and the fact that with a pure covalent EuX -bond ($j_p = 0$) the attributed (extrapolated) h. f. field corresponds to that of the $4f^7 6s 6p$ configuration suggests bonding p- and s-electrons being shared nearly equally between Eu and X. However, comparing the branches «S» and «B» with J_1 and J_2 in figure 1b, a correlation of J_1 with «S» and of J_2 with «B» is cogent. This suggests the increase of term ($A_{ce}^s S$)_{*i*} on branch B to be related to increasing overlap and transfer between anion p- and cation 5d-e_g-orbitals causing both the bonding and the superexchange J_2 . The increasing s-electron density at the Eu nucleus on branch «S» equivalently would be related to the increasing overlap of 5d-t_{2g} orbitals between neighbouring Eu atoms thus causing additional bonds together with the exchange interaction J_1 . The participation of 5d-t_{2g} orbitals in bond and exchange would decrease the shielding of the outer Eu-s-electrons and hence cause the observed increase of $L_s(0)$.

To summarize: Strong correlations between the h. f. interactions, electron densities and nature of bonds, band structures, and exchange interactions have been detected by the systematics proposed and discussed here and are waiting for further experimental checking and an improved theoretical understanding now.

2. ¹⁶⁶Er/Er³⁺ h. f. interactions in Er-Al intermetallic compounds. — 2.1 SIGNIFICANT RELATIONS FOR ¹⁶⁶Er/Er³⁺ H. F. INTERACTIONS. — In this section we will discuss recent M. E. studies with a typical non S-state rare-earth ion, Er³⁺, which demonstrate that the usual neglect of transferred h. f. fields is not justified in intermetallic compounds of heavy rare-earths such as Er.

(3) Note, that by relying on «S» and deducing δ_{is} from the magnetic h. f. splittings the experimental error of δ_{is} would be due to ΔB_{2f} instead of $2 F_{ex}$ (shown in fig. 2) and thus could be reduced.

$J = L + S$ now is expected to be a good quantum number. The Er³⁺ groundstate is $4f^{12} - ^4I_{15/2}$ ($L = 6, S = 3/2, J = 15/2$) and corresponds to a magnetic moment $\langle \mu \rangle = g_J \mu_B \langle J_z \rangle$, where g_J is the Lande factor ($g_J = 6/5$ with Er³⁺). $\langle J_z \rangle$ again is the thermal average over the $2J + 1$ eigenstates of J_z responsible for the temperature dependence of the magnetization as given by

$$m(T) = \langle J_z \rangle / J = \text{Tr}(J_z \rho) / J \text{Tr} \rho, \quad \text{where}$$

$\rho = \exp(-J_z g_J \mu_B H_{\text{eff}}(T) / kT)$ is the density matrix for the molecular field ($H_{\text{eff}}(T)$) approximation.

The h. f. field given by eq. (1) is to supplement now by another contribution

$$B_{4f} = A_{4f} \langle J_z \rangle \quad (3)$$

resulting in a total field of

$$B_{1,i} = [A_{4f} + (g_J - 1)(A_{\text{core}}^s + A_{\text{ce}}^s)]_i \langle J_z \rangle_i + \sum_{j \neq i} [A_{\text{ce}}^s (g_J - 1) + A_{\text{val}}]_j \langle J_z \rangle_j. \quad (3a)$$

Since $A_{4f} \approx 100$ T, B_{4f} is the dominating contribution here, whereas the A_i^s give rise to only a correction of a few percent and A_j so far has been assumed negligible. We will see, however, that this is not admissible generally, since in certain cases $A_j / A_{4f} \sim 0.05$ may be obtained. For the temperature dependence (under the presumptions made already with S-states) again

$$B_{1,i}(T) / B_{1,i}(0) = H_{\text{eff}}(T) / H_{\text{eff}}(0) = M_i(T) / M_i(0) = \text{Tr}(J_z \rho) / J \text{Tr} \rho$$

is expected to hold. In addition to the case of S-states the term B_{4f} is always accompanied by an temperature dependent electric field gradient (e. f. g.) at the r. e.-nucleus. It is given by

$$q_{4f}^{zz}(T) / q_{4f}^{zz}(0) = \text{Tr} \{ [3 J_z^2 - J(J + 1)] \rho \} / \text{Tr} \rho / (2J - 1) J \quad (4)$$

and exists also with cubic lattice symmetry, where the lattice term $q_{\text{latt}}(1 - \gamma_\infty)$ of the total e. f. g.,

$$q = (1 - R_Q) q_{4f} + (1 - \gamma_\infty) q_{\text{latt}},$$

vanishes (R_Q and γ_∞ are Sternheimer's shielding and antishielding factors [2]). Using an operator equivalent method B_{4f} and q_{4f} have been calculated by Elliot and Stevens [2, 28] to

$$B_{4f}^z = 2 \mu_B \langle 4f / r^{-3} / 4f \rangle \langle J // N // J \rangle \langle J_z \rangle \quad (3b)$$

$$q_{4f}^{zz} = -e \langle 4f / r^{-3} / 4f \rangle \langle J // \alpha // J \rangle \times \langle 3 J_z^2 - J(J + 1) \rangle. \quad (4a)$$

The matrix elements of r^{-3} , N , and α are tabulated [2, 28] and yield $10.60 \times a_0^{-3}$, 0.78, and $1/400$, respectively, for Er³⁺.

For the 80.6 keV ($2^+ - 0$) transition used in ¹⁶⁶Er M. E. experiments (see Table 1) the energy of the five transitions ($m_I = -2, -1, \dots, +2$) are given by

$$\Delta E(m_I) = E(m_I) - E_0 = A m_I + 3 P (m_I^2 - 2) \quad (5)$$

where from eq. (3), (4), and table 1 the relations between the magnetic and quadrupole coupling

constants (A and P , respectively) and $B_{1,i}(0)$ or $\langle J_z \rangle_0$ can be calculated to

$$A_{4f}(0)/(\text{cm/s}) = 3.6465 \times 10^{-3} B_{4f}(0)/(T) = 0.374 \langle J_z \rangle_0 = 0.312 \langle \mu_z \rangle_0 / (\mu_B)$$

and

$$P(0)/(\text{cm/s}) = eQq_{zz}/24 = 6.27 \times 10^{-4} \langle 3J_z^2 - J(J+1) \rangle_0.$$

We are interested in $\langle J_z \rangle_0$ for Er^{3+} at a given lattice site with cubic symmetry here, i. e. in cubic Laves-structures RX_2 (space group $\text{Fd } 3\text{m-O}_h^7$, $\text{MgCu}_2\text{-C } 15$ -type) and in cubic RX_3 -structures (space group $\text{Pm } 3\text{m-O}_h^1$, $\text{Cu}_3\text{Au-L1}_2$ -type).

In RX_2 each R is surrounded tetrahedrally by four R-n. n. being e. g. in ErAl_2 0.337 nm apart. In RX_3 each R is surrounded by twelve X-n. n. being (with ErAl_3) 0.298 nm apart from R while the six R-n. n. n. form an octahedron and are 0.421 nm apart. Hence, the transferred h. f. fields, if any, in RX_3 would be expected to be smaller than in RX_2 . In both cases we have R^{3+} in cubic symmetry. Thus, due to LEA [29] after splitting of the Er^{3+} groundstate J-manifold by the crystal field (c. f.) a Γ_8 -quartet or a Γ_6 -doublet is expected to lie lowest with ErAl_3 and ErAl_2 , respectively. The lower limit of $\langle J_z \rangle_0$ and $\langle \mu \rangle_0$ then are the Γ_8 -values, i. e. $\langle J_z \rangle_0 = 4.6$ and $\langle \mu \rangle_0 = 5.5 \mu_B$. This presumes the c. f. splitting Hamiltonian (\mathcal{H}_{CF}) to be large with respect to the magnetic exchange splitting

Hamiltonian (\mathcal{H}_{M}). For the other limit, $\mathcal{H}_{\text{M}} \gg \mathcal{H}_{\text{CF}}$, the usual, equally spaced $(2J+1)$ -multiplet is expected with $\langle J_z \rangle_0 = -J = -15/2$ lying lowest and yielding $\langle \mu \rangle_0 = 9 \mu_B$. This groundlevel is also expected with a splitting into eight Kramers doublets in a non-cubic c. f. where $|\pm 15/2\rangle$ is lowest in energy.

In figure 3 the ^{166}Er M. E. spectra for pure and Y-substituted Er-Al-compounds are shown [30, 31] for the lowest temperatures used. Between ErAl_2 and ErAl_3 apparently the h. f. splittings differ by nearly a factor 2 and so do the T_c -values and the $\langle \mu \rangle$ -data deduced from the M. E. spectra by means of eq. (3) to (5). Substitution of Er by Y causes a pronounced decrease of T_c and $B_{1,i}$ (i. e. $\langle \mu \rangle_i$) as can be seen from figures 3 and 4. In addition, significant line

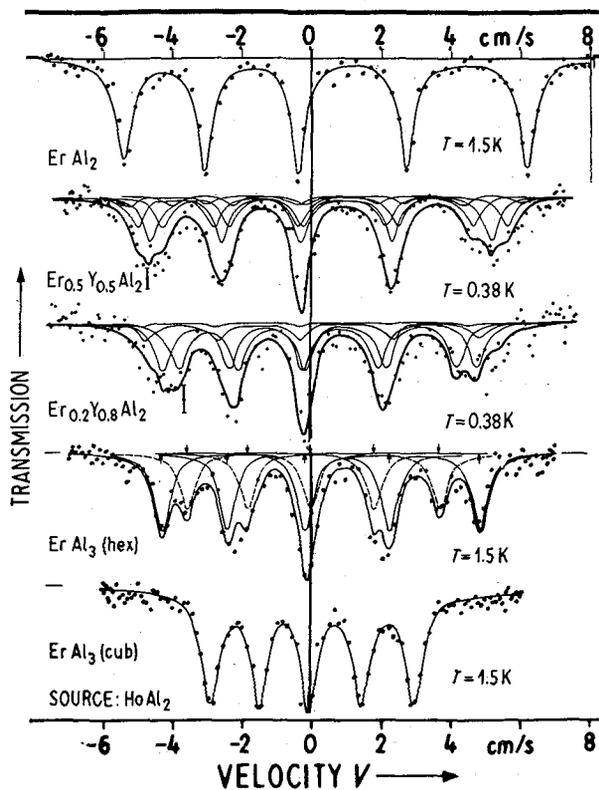


FIG. 3. — ^{166}Er M. E. spectra of different Erbium-Aluminium intermetallic compounds. (With $\text{Er}_{1-x}\text{Y}_x\text{Al}_2$ spectra for $n_1 = 0, 1, \dots, 4$ Y-n. n., and with $\alpha\text{-ErAl}_3$ with two sublattices are drawn. Typical Er^{3+} spin relaxation effects have been observed at highest temperatures only as analyzed in [30,31] and can be ruled out for the low temperature spectra shown here.)

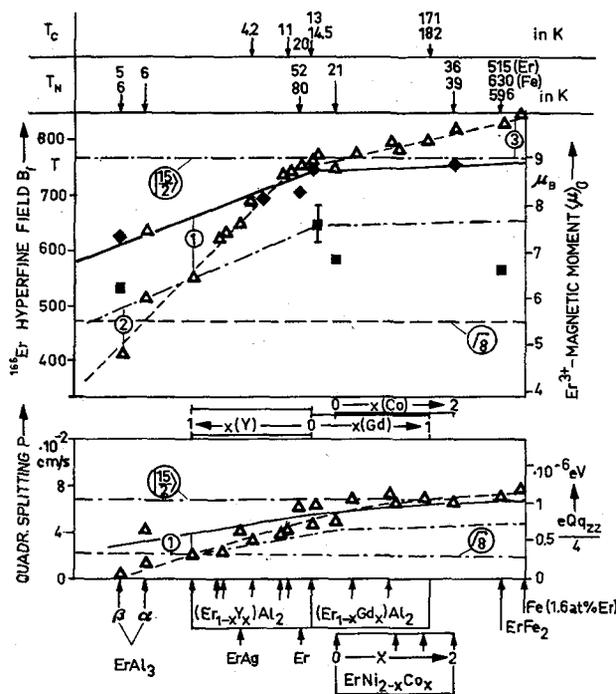


FIG. 4. — Summary of Er^{3+} -magnetic moments obtained from neutron diffraction (\blacklozenge), bulk magnetization measurements (\blacksquare), and comparison with ^{166}Er h. f. data (\blacktriangle). Proposed corrections for Er-Er and Er-X (X: Co, Fe) transferred h. f. fields are labelled (1) (2) and (3), respectively. Abscissa is the substitution x in $(\text{Er}_{1-x}\text{X}_x)\text{Al}_2$ (X: Y, Gd). The systematics of h. f. data revealed by these two series of Laves-structures by the drawn lines have been used to locate abscissa for the other examples with respect to their splitting data.

broadenings and structures are revealed. They are due either to changes of the intrinsic B_1 -term because of different moments $\langle \mu \rangle_i$ or to changes of the sum-term of the transferred h. f. fields, both caused by the now given distribution of different local Er-Y-environments. The same question arises with the two inequivalent sublattices displayed by $\alpha\text{-ErAl}_3$ [32, 33]. Neutron diffraction data on $\langle \mu \rangle_0$ are required to distinguish between the two possibilities and are under way. The so far available results are plotted in figure 4 [34, 35]. In α - and $\beta\text{-ErAl}_3$ and in $\text{Er}_{1-x}\text{Y}_x\text{Al}_2$ the $B_1(n_1)$ and $q_{4f}^{zz}(n_1)$ data attributed to $n_1 = 0, 1, 2, 3$, and 4 Er-n. n. substituted by Y have been deduced from these M. E. spectra by means of a computer

fit [30, 31]. The results are plotted in figure 4 against the Er-substitution x . In order to reveal possible systematics of the h. f. data, in figure 4 related and significant $^{166}\text{Er}/\text{Er}^{3+}$ h. f. data have been compiled, e. g. the data obtained by Purwins [36] on the $\text{Er}_{1-x}\text{Gd}_x\text{Al}_2$ series and by Petrich [37] on $\text{ErNi}_{2-x}\text{Co}_x$ compounds. The distinct ErX_2 -families have been located on the abscissa in such a way that B_1 , P , $\langle \mu \rangle$ and $T_{c(N)}$ increase monotonously from the left to the right. In addition the results by Hüfner [38] on Er-metal, by Cohen [39] on ErFe_2 , and by Weber [40] on 1.5 % Er diluted in b. c. c. iron are included. The $\langle \mu \rangle$ -data deduced from the M. E.-data are to be compared with recent results of bulk magnetization measurements available with ErAl_2 [36, 41, 42], ErAl_3 [43], $\text{ErNi}_{2-x}\text{Co}_x$ [37, 44], ErFe_2 [45], partially reviewed already by Bozorth [46]. In compounds displaying a ferrimagnetic or still more complicated spin structures it is meaningful to compare the M. E. results with $\langle \mu(\text{Er}) \rangle$ deduced from neutron diffraction (N. D.) studies rather than with bulk magnetization. Recent N. D. data available for $\beta\text{-ErAl}_3$, $\text{Er}_{0.5}\text{Y}_{0.5}\text{Al}_2$ [35], ErAl_2 [34], ErCo_2 [47], and Er [48] are plotted in figure 4. As a rule, the microscopic methods so far yielded much higher $\langle \mu \rangle$ -values than bulk magnetization measurements.

In fact, as in the case of Eu-compounds, the compilation of magnetic and h. f. data in figure 4 again reveals certain systematics and correlations, which lead us to some significant conclusions on intrinsic and transferred h. f. interactions: *a*) As expected, it becomes obvious from figure 4 that the influence of the c. f. and attributed quenching of $\langle \mu(\text{Er}) \rangle$ increase from the right to the left side with decreasing $T_{c(N)}$ and hence decreasing magnetic exchange splitting of the J-manifold. *b*) The slope of $\langle \mu \rangle$ against substitution x revealed by the N. D. data is much smaller than that observed with the h. f. fields and attributed $\langle \mu \rangle$ -values. Hence, the variations of $\langle \mu \rangle$ revealed by N. D. data can only partially account for either the observed decrease of B_1 with magnetic dilution of the Er-sublattice by Y or for the enhanced increase of B_1 with substitution of the non-magnetic X atoms (e. g. Al) by transition elements (e. g. Fe, Co). Thereby, the remaining ΔB_1 have to be attributed to transferred h. f. fields. In $\text{Er}_{1-x}\text{Y}_x\text{Al}_2$ these transferred h. f. fields at an central Er-atom with all four Er-n. n. substituted by Y (labelled ① in Fig. 4) are found to be about 120 T, i. e. $\Delta B_1 = 30 \text{ T}/(\text{Er n. n.}, 0.337 \text{ nm apart})$. Hence, if one attributes this reduced B_1 -value ($770 - 120 = 550 \text{ T}$) to the intrinsic term (« i ») in eq. (3) (i. e. to the contribution which in fact is related to $\langle \mu \rangle$ by the eq. (3) to (5)) then one can again draw a base-line for this term, which runs parallel to that obtained for the N. D. data. The M. E. data for $\langle \mu \rangle$ deduced from these separated intrinsic fields

$B_{1,i} \approx B_{4f,i}$ then are seen to be much smaller than those deduced so far from B_1 instead $B_{1,i}$. The $\langle \mu \rangle$ now are closer to the bulk magnetization values than to the N. D.-data. They further reveal considerable c. f. quenching of $\langle \mu \rangle$ for all examples and show that with $\beta\text{-ErAl}_3$ the Γ_8 -c. f. value for $\langle \mu \rangle$ is nearly obtained. Note that with this example the transferred h. f.-field of -80 T (labelled ②) has changed sign and yields $\Delta B_2 \approx -13 \text{ T}/(\text{Er n. n.}, 0.421 \text{ nm apart})$. The transferred h. f. fields due to the substitution of Al by Co or Fe (labelled ③) reach about $+64 \text{ T}$ for Er in b. c. c. Fe, i. e. $\Delta B_3(\text{Fe}) \approx 8 \text{ T}/(\text{Fe-n. n.})$.

The mechanism responsible for such large ΔB_j is still unknown. However, since the quadrupole splittings P shown in figure 4 reveal the same behaviour as B_1 just discussed, and, in particular, since also transferred e. f. gs.

q_j^{zz} are indicated, at least with the Er-substitutions s-electron spin-polarization seems to be ruled out. On the other hand, spin-orbit-couplings between conduction electrons and the rare-earth cations have been shown by Levy [49] to be significant and necessary for the understanding of the T_c -systematics of the RX_2 -series of compounds. In fact, this mechanism could account also for ΔB_1 and ΔB_2 . The contributions ΔB_3 have been observed previously between GdAl_2 and GdFe_2 by Gegenwarth [50] and related to valence electron polarization. In any case, the ΔB_j are again found to be significant and closely related to bonding and exchange contributions by electrons, which display either p- or d-character.

Conclusion. — For two typical cases, i. e. $^{151(153)}\text{Eu}/\text{Eu}^{2+}$ (S-state) in EuX and $^{166}\text{Er}/\text{Er}^{3+}$ (J-groundstate) in Er-intermetallic compounds, it has been shown that significant transferred h. f. interactions exist. They necessitate a reanalysis of the conclusions made so far on Er^{3+} ionic magnetic moments and enable one to separate between intrinsic and transferred h. f. interactions. Taking this into account systematics for both contributions can be established. The intrinsic part is shown to be related to the ionic moments while the transferred contributions and isomer shifts are shown to be closely correlated mutually and with the nature and strength of bonds and exchange interactions. This opens new possibilities for using the M. E. as a microscopic tool for the study of bonds and interactions in magnetically concentrated and ordered solids.

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