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MEASUREMENTS OF MAGNETIZATION DENSITIES IN RARE-EARTH COMPOUNDS

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Résumé.— Les neutrons polarisés sont un outil unique pour étudier l'état électronique des terres rares et de leurs composés. Les neutrons à courte longueur d'onde sont particulièrement adaptés vu les problèmes d'extinction et vu aussi l'extension spatiale du facteur de forme dans l'espace réciproque. C'est à travers la densité d'aimantation, qui elle-même est directement "vue" par les neutrons, que l'on détermine l'état fondamental de la terre rare. On le compare ensuite avec les résultats de calculs provenant de modèles où sont inclus champ cristallin et échange. Ces comparaisons ont montré la nécessité dans certains cas d'inclure dans le mécanisme d'échange des termes d'ordre supérieur qui vont au delà de l'approximation du champ moléculaire. Un moment magnétique dû à la polarisation des électrons 5d par le moment 4f a aussi été mis en évidence. Il a pour origine des interactions avec le spin des électrons 4f, mais aussi avec leur orbite. Dans le cas des terres rares anormales où cette aimantation 5d joue un rôle primordial, les expériences de neutrons polarisés sont essentielles pour comprendre leurs propriétés.

Abstract.— Polarized neutrons are a unique tool for studying the electronic state of rare earth metals and rare earth compounds. Due to extinction problems and also due to the large extension of rare earth form factors in reciprocal space, hot neutrons are most suitable. Through the magnetization density which is directly measured with neutrons, the ground state of the rare earth is directly determined. It can be compared to results of calculations performed with models including crystal field interactions and exchange interactions. Such comparisons show the need in certain cases of high order terms in exchange mechanism which go beyond the molecular field approximation. The existence of a 5d moment, polarized by the localized 4f magnetization is also demonstrated. The study of such conduction electron moments is expected to be helpful in the understanding of abnormal rare earth behaviour in metals and rare earth compounds.

1. Introduction

The lanthanide series provides a large field of investigation for the study of magnetism. The magnetic properties of the rare earth ions are due to the inner incomplete 4f shell, whose electrons are tightly bound inside outer closed shells. An important associated screening by outer electrons makes the influence of the environment rather weak. As a result, the Coulomb correlation energy of the 4f electrons requires a localized description, even in metals, and the ground state is given by Hund's rules. Also, the perturbation of the crystalline electric field (CEF) is small compared to the spin-orbit coupling. Thus the ions are described in terms of a total angular momentum J.

Among the methods used for a study of rare earth magnetism, the direct observation of the spatial distribution of the magnetization density is very meaningful. This microscopic approach can provide a direct picture of the state of the 4f ion which results from competition between CEF and magnetic interactions. Furthermore the magnetization density measurement is the only way to reach and to analyze the additional contribution which is due to the conduction electrons. This density, present in metals and alloys, is more delocalized than that of the 4f one, and mediates indirect magnetic interactions.

2. 4f form factor : Measurements and formalism

a) Polarized neutron experiments

Neutron scattering allows the measurement of the magnetic structure factors $F_M(\vec{H})$ which are the Fourier components of the magnetization density. For accurate measurements of small $F_M(\vec{H})$, polarized neutrons are needed : the essential advantage of this technique arises from the interference term occurring between nuclear and magnetic scattering. Moreover, the measurement of the flipping ratio R ($R = I^+/I^-$), between scattered intensities for the two possible neutron polarization of the beam, yields directly the value of the ratio $\gamma = F_M(\vec{H})/F_N(\vec{H})$ without any normalization factor.

When considering measurements of rare earth form factors, especially in alloys or compounds, some specific experimental difficulties emerge :

i) Due to the high localization of the magnetization density, the form factor is greatly expanded in reciprocal space. In order to get a sufficient set of observations, measurements of Bragg reflections at large $\sin \theta/\lambda$ values are needed which can only be obtained with neutrons of short wavelength.

ii) The accuracy of polarized neutron experiments is essentially limited by extinction phenomena. Moreover, rare-earth compounds are often brittle and it is not possible to reduce extinction effects by induced mechanical straining of the samples. To overcome this difficulty, measurements of flipping ratios are performed at several short wavelengths (between 0.9 Å and 0.4 Å) which minimizes extinction effects. Furthermore extrapolation of the data to $\lambda = 0$ permits the determination of extinction free values.

iii) Another limitation in the accuracy of the measurements of the magnetic structure factors $F_M(\vec{H}) = \gamma F_N(\vec{H})$ arises from the lack of exact knowledge of the nuclear structure. In particular, it is essential to determine the scattering length of the rare-earth nucleus, value which may be affected by the proximity of resonant absorption peaks, and by nuclear polarization :

$$b(\lambda) = b_0 + \Delta b'(\lambda) + i \Delta b''(\lambda) + f_N \frac{\vec{\sigma} \cdot \vec{B}}{B_0} \quad (1)$$

Besides the value of b_0 which often is not well known, there are extra terms which are wavelength dependent. These can be calculated from absorption data, using the Breit-Wigner [1] formulae. Moreover, the very large hyperfine fields at the rare-earth nuclei, which originate from the large electronic orbital contributions, can polarize, even at 4.2K, a sizeable part f_N of the nuclear moment if the nuclear spin $\vec{I}$ differs from zero. This polarization leads to coherent scattering arising from the nuclear pseudomagnetic term.

In summary, measurements at different and short wavelengths appear to be very important in order to complete the measurements and to treat extinction. It is worth noticing also, that for important magnetic elements such as samarium and gadolinium, absorption is considerably reduced at short wavelengths. This allows measurements on related compounds to be performed with natural elements. The facilities available at the ILL, thanks to the hot source, have stimulated numerous studies.

b) Formalism of atomic 4f form factors

The localized character of the 4f electrons permits atomic calculations to be used for their description. In the case of rare-earth ions, the magnetic scattering involves both spin and orbit contributions. The spin-orbit coupling being large compared to CEF interactions, the ion must be described in terms of a total angular momentum J . The perturbing effect of a crystal field or a magnetic field is to remove the $2J+1$ degeneracy of the ground multiplet. The wave-functions are given as

$$\psi = R(\vec{r}) \sum_M a_M |JM\rangle \quad (2)$$

With this hypothesis, the calculation of the magnetic amplitudes $\vec{F}_M$ may be performed by the tensor-operator method [2,3], using Racah algebra. The vector $\vec{F}_M$ is given by its spherical components F_{M_0} , F_{M_1} , $F_{M_{-1}}$.

$$F_{M_q}(\vec{H}) = \frac{\gamma e^2}{mc^2} \sqrt{4\pi} \sum_{K''Q''} Y_{Q''}^{K''}(\hat{H}) \sum_{K'Q'} \sum_{MM'} a_M^* a_{M'} \left[A(K''K') + B(K''K') \right] \langle K'Q'JM' | JM \rangle \times \langle K''Q''K'Q' | 1q \rangle \quad (3)$$

In this formula $Y_{Q''}^{K''}(\hat{H})$ depends on the two angles Θ and Φ which represent the direction of the scattering vector $\vec{H}$. $A(K'',K')$ and $B(K'',K')$ represent respectively the orbital and the spin contribution to the scattering. They can be calculated using tabulated coefficients for the rare earths [4] and the radial integrals

$$\langle j_{K'}(\vec{H}) \rangle = \int dr r^2 |\vec{R}(r)|^2 j_{K'}(Hr) \quad (K' = 0, 2, 4, 6) \quad (4)$$

Considering that the magnetic amplitude is a vector, the cross-section for polarised neutrons is

$$F_N(\vec{H})^2 + 2 F_N(\vec{H}) F_{M_0}(\vec{H}) + \left[F_{M_0}(\vec{H})^2 + 2 |F_{M_1}(\vec{H})|^2 \right] \quad (5)$$

the usual ratio

$$\gamma = \frac{F_{M_0}(\vec{H})/\sin^2\Theta}{F_N(\vec{H})} \quad \text{may only be defined}$$

when the following relation is fulfilled :

$$F_{M_0}(\vec{H})^2 = \sin^2\Theta \left[F_{M_0}(\vec{H})^2 + 2 |F_{M_1}(\vec{H})|^2 \right] \quad (6)$$

This is the case, or nearly, in most of the experimental situations [5].

3. Electron, spin and magnetization densities

We examine in this section, the sort of results which neutron experiments can provide in the case of 4f magnetism. As the orbital momentum L generally differs from zero, different orbitals are involved. In addition, the orbital moment being unquenched, an important contribution to the moment appears and its localization differs from that of a spin density. Also, the large value of the spin-orbit coupling implies that the spin-density is a combination of different spin-states. Thus, in general, the magnetization density differs from the spin density and the latter, unlike the case of 3d electrons, is also different from the electronic density. However, in the case of gadolinium where the 4f shell is half filled, these 3 densities are equivalent.

a) Case of an S-state : Gadolinium

The 4f shell is half-filled, containing seven electrons, and the orbital moment is zero. The magnetization density is spherically symmetrical ($\psi(\vec{r}) = R(r)$). The measurement of the magnetic form factor allows a direct determination of the 4f electron distribution. The comparison of experimental form factors with radial integrals $\langle j_0(H) \rangle$ calculated in atomic models constitutes a test for these models.

		L	S	J	g_J	g_{J^2}	C_2 dip	saturated ion		
								magnet.	spin	electron
Ce ³⁺	f ¹	3	1/2	5/2	6/7	2.14	1.600	0	0	0
Pr ³⁺	f ²	5	1	4	4/5	3.20	1.644	P	0	0
Nd ³⁺	f ³	6	3/2	9/2	8/11	3.27	1.803	P	0	0
Pm ³⁺	f ⁴	6	2	4	3/5	2.4	2.263	P	P	P
Sm ³⁺	f ⁵	5	5/2	5/2	2/7	0.71	5.422	0	P	P
Eu ³⁺	f ⁶	3	3	0	no moment		-			
Gd ³⁺	f ⁷	0	7/2	7/2	2	7.0	0			
Tb ³⁺	f ⁸	3	3	6	3/2	9.0	0.370		P	0
Dy ³⁺	f ⁹	5	5/2	15/2	4/3	10.0	0.533	P	P	0
Ho ³⁺	f ¹⁰	6	2	8	5/4	10.0	0.613	P	P	0
Er ³⁺	f ¹¹	6	3/2	15/2	6/5	9.0	0.652	P	0	P
Tm ³⁺	f ¹²	5	1	6	7/6	7.0	0.667	0	0	P
Yb ³⁺	f ¹³	3	1/2	7/2	8/7	4.0	0.667	0	0	P

Table 1 : Rare-earth characteristic quantum numbers, orbital coefficients C_2 (dipole approximation) and asphericity of the electron spin and magnetization density (0 = oblate, P = prolate).

In gadolinium metal [6], the radial dependence of the 4f density appears to be significantly expanded with respect to classical Hartree-Fock calculations [7]. A good agreement can only be achieved using relativistic methods [8] (Dirac-Fock). The expansion of the 4f radial density has been explained as an indirect relativistic effect, the relativistic contraction of the core electrons resulting in a more effective screening of nuclear charge. These relativistic calculations [9] appear to be the best adapted to all the other studies of rare earth form factors where a comparison have been performed.

b) Orbital contribution : spatial extension of the magnetization density.

A large orbital contribution to the magnetic moment is associated with an open 4f shell. The orbital magnetization density which corresponds to a moment created inside the electron orbitals is more localized than the spin density.

As a first approximation both these densities can be assumed to be spherically symmetrical (dipole approximation). Considering only the spherical term in the relation (3), leads to

$$|F_M(\vec{H})| = \mu \left[\langle j_0(H) \rangle + c_2 \langle j_2(H) \rangle \right]$$

where the values of the coefficients c_2 which characterize each ion are tabulated in table I.

The orbital contribution drastically changes the spatial extension of the magnetization density compared to the case of spin density only. Therefore the form factors for rare earth elements with an orbital moment are more expanded in the reciprocal space than the Gd form factor. Also, the form factors are different from light and heavy rare-earths. This property is illustrated in Figure 1 where rare-earth form factors measured in different RAI_2 alloys appear. For R elements of the first half the form factor is more expanded than for elements of the second half. In fact, when $J = L-S$, the total magnetization density results from a partial cancellation between the orbital density (more localized) and the spin density (less localized).

This behaviour is emphasized in the case of samarium where $S = 5/2$ and $L = 5$. The values of the spin and orbital moments are very close : the form factor exhibits a maximum for a value of $\sin \theta / \lambda$ which is different from zero [10, 11] (Figures 1d and 2). In $SmCo_5$ [12] at 4.2K the Sm moment has a dominant orbital character and reaches $0.38 \mu_B$. An interesting property is observed which essentially results from a mixing of higher J multiplets into the ground multiplet : the form factor is largely temperature dependent. When excited levels, presenting a dominant spin character, become populated, the peak shape of the Sm form factor is enhanced. At 300 K, the Sm moment has decreased to $0.04 \mu_B$. A cross-over temperature, at which the spin moment exactly cancels the orbital moment, has been calculated to occur at 350K. As the coupling between the cobalt moment (which is almost a spin moment) and the rare earth spin is always antiferromagnetic below this temperature $SmCo_5$ is a ferromagnet and above this temperature, it is a ferrimagnet.

c) Anisotropies of the spin and magnetization densities

The angular dependence of the 4f electrons must be described, as already mentioned, on the $|JM\rangle$ basis, the elements of which are not spherically symmetrical. In the simple case of only one electron in the 4f shell (Ce^{3+} ion) the asphericity is extreme and is illustrated below. The $|5/2, M\rangle$ wave function results from the coupling of an orbital moment $\ell = 3$ and of a spin $s = 1/2$ leading to a total moment $J = j = 5/2$

$$|5/2, M\rangle = \left(\frac{7/2-M}{7}\right)^{1/2} Y_{M-1/2}^3(\hat{r}) \chi(1/2) + \left(\frac{7/2+M}{7}\right)^{1/2} Y_{M+1/2}^3(\hat{r}) \chi(-1/2)$$

The corresponding angular probability of occupation is shown as a polar diagram in figure 3. In the case of cerium it is equivalent to the angular part of the magnetization density. Very different angular dependences are associated with the

Fig. 1: Rare-earth magnetic amplitudes in RAl_2 compounds (ref. 17,18,19,26,36)

Fig. 2 : Samarium magnetic amplitudes at 4.2K and 300K in SmCo₅ (ref. 12).

The dashed line corresponds to the saturated state $|5/2, 5/2\rangle$ and the full line to the level scheme.

Fig. 3 : Polar diagrams for the angular probability of occupation (full line) and angular spin density (dashed lines) of the $|5/2, M\rangle$ basis states of Ce³⁺.

different states, and consequently different form factors (Fig. 4). The spin densities which are also represented in Figure 3 are, as already mentioned, different from electron and magnetization densities.

With large exchange interactions, the rare earth ions are in their saturated state $|JJ\rangle$. The density exhibits axial symmetry, and is either elongated (prolate) or contracted (oblate) along the symmetry axis. In such a case, the form factor is dependent only on the angle θ between the z-axis and the scattering vector. The cerium form factors associated with the state $|5/2, 5/2\rangle$ for $\theta = 90^\circ$ and $\theta = 30^\circ$ are very different and differ also from the spherical form factor (Fig. 5). The associated magnetization density is oblate (see fig. 3a).

Fig. 4 : Ce^{3+} form factors ($\theta = \frac{\pi}{2}$) for the different $|5/2, M\rangle$ basis states as well as for the dipole approximation.

Fig. 5 : Ce^{3+} form factors of the $|5/2, 5/2\rangle$ basis state for different azimuthal θ angles as well as for the dipole approximation.

The asphericities of the magnetization density for the $|JJ\rangle$ states of the rare-earth elements obtained by considering only second order terms are summarized in Table I. They are compared to those of the spin density and to those of the electron density as deduced from the sign of the Stevens coefficients. The asphericities of spin and magnetization densities may differ due to the influence of the orbital moment. The asphericities of spin and electron densities are the same for light rare-earths and opposite for heavy rare-earths. As a first approximation the spin density reflects the electron density, but for heavy rare earths where the 4f shell is more than half-filled it is representative of unpaired electrons.

4. 4f form factor and 4f wave function

In this section we give some examples to show how the 4f form factor is connected to the 4f electron wave-function which, in turn, reflects exchange and CEF interactions.

a) Description of the observed form factors

At low temperatures, the observed form factor is characteristic of the ground state which is the only state populated. In rare-earth metals where the crystalline symmetry is hexagonal, dominant exchange interactions determine the ground state to be that of the saturated ion $|JJ\rangle$ as already mentioned.

The magnetization density and therefore the associated form factor have a cylindrical symmetry with respect to the magnetization axis. The magnetic amplitudes measured in the equatorial plane exhibit a smooth decrease versus $\sin \theta/\lambda$ [13,14]. The asphericity of the magnetization density was shown directly in the case of Tm metal [14] (where it is oblate) by measurements of Bragg reflections out of the equatorial plane. It is worth noticing, although never experimentally measured, that in such a case, due to the strong spin-orbit coupling, the magnetization density would reorientate along any direction under an applied magnetic field high enough to overcome magnetocrystalline anisotropy. This is unlike the case of 3d magnetism, where very large crystal-field effects determine the 3d orbitals and lead to a quenching of the orbital moment. The magnetic moment freely orientates along an applied field without modification of the spin-density.

When the exchange interactions are weak, the states of the 4f electrons are essentially determined by crystal field effects. In TmSb, where exchange interactions can be neglected, the ground state is a non-magnetic singlet [15]. A magnetic moment of $1.2 \mu_B$ is induced by an applied magnetic field of 12.5 kOe. As expected in cubic symmetry for a low field, this value does not depend on the field direction. However, the magnetization density exhibits 4-fold or 2-fold symmetry depending on whether the field is applied along [100] or [110]. This leads, as observed by LANDER et al. [16] to different anisotropies of the Tm form factor for different field directions.

In many cases, crystal field and exchange interactions are competing. The larger the crystalline electric field compared to the exchange interactions, the more closely will the symmetry of the magnetization density reflect the crystal symmetry. A typical example is that of cerium where there is only one electron on the 4f shell and the magnetization density may be highly anisotropic. The form factor measured in the Laves phase compound CeAl_2 [17] at 1.5K under an applied field of 46 kOe parallel to [110] is shown in Fig. 1a. The points are considerably scattered and reveal a projection of the magnetization density elongated along the 2-fold axis in the plane perpendicular to the field direction. Such a shape is characteristic of a Γ_7 -like state, although the quantitative analysis shows that mixing with the Γ_8 state of higher magnetization occurs, induced by exchange interactions.

b) Determination of the 4f ground state

Analysis of the magnetic amplitudes at low temperature allows a determination of the 4f ground state. Such studies are simpler in cubic compounds such as RAl_2 or RZn where only R atoms are magnetic. Except at low $\sin \theta/\lambda$ values, where conduction electron polarization is present (see next section), it may be assumed that only 4f magnetism contributes to the observed magnetic amplitudes. A reduction of the 4f moment compared to that of the saturated state $|JJ\rangle$ appears systematically. This gives evidence for CEF mixing of different $|JM\rangle$ states. The associated symmetry of the ground state wave function is reflected in the selection rules which determine it: $\Delta M = n$, where n is the order of symmetry of the magnetization axis. For example, in the cubic Laves phase NdAl_2 [18], the easy direction of magnetization is the 4-fold axis, the ground state wave function may, a priori, be written as :

$$|\psi_{\text{Nd}}\rangle = a_{9/2} |9/2, 9/2\rangle + a_{1/2} |9/2, 1/2\rangle + a_{-7/2} |9/2, -7/2\rangle$$

where the a_M 's are the only unknown parameters to be determined from the experiment, as far as the radial integrals $\langle j_K \rangle$ can be taken from atomic calculations. The wave function which fits best the data is :

$$|\psi_{\text{Nd}}\rangle = 0.88(8) |9/2, 9/2\rangle + 0.45(8) |9/2, 1/2\rangle - 0.11(18) |9/2, -7/2\rangle.$$

The overall agreement between experimental and calculated magnetic amplitudes is excellent (Fig. 1c). The Nd moment deduced from these measurements reaches $2.61 \mu_B$.

In RFe_2 (cubic Laves phase) and RCo_5 (hexagonal CaCu_5 type structure) compounds, 3d and 4f magnetism coexist. In this case, analysis of the data is more complex since the 3d magnetic contribution must be subtracted from the 4f contribution. The Sm form factor measured in SmCo_5 [12] at 4.2K is shown in Figure 2. The peak shape of the form factor, characteristic of the Sm ion is as already mentioned even more pronounced than for the state $|5/2, 5/2\rangle$ of maximum magnetization when considering only the ground multiplet. As in SmAl_2 [19] and SmZn [20], exchange interactions, increase the spin contribution to the magnetization moment through mixing with the excited multiplets [11, 12]. The wave function fitted by considering only the first excited multiplet $J = 7/2$ may be written as :

$$|\psi_{\text{Sm}}\rangle = 0.978 |5/2, 5/2\rangle + 0.205 |7/2, 5/2\rangle$$

In NdCo_5 or HoFe_2 , since exchange interactions are much larger than CEF interactions, the rare-earth form factor is expected to be that of the saturated ion. In fact, as shown in Fig. 6, the extrapolation to $\sin \theta/\lambda = 0$ leads in HoFe_2 [21][22] to a 4f moment of $9.15 \mu_B$, the ground state wave function being

$$|\psi_{\text{Ho}}\rangle = 0.90 |8, 8\rangle + 0.43 |8, 4\rangle + 0.00 |8, 0\rangle$$

It is worth noticing that recent NMR measurements in several RFe_2 inter-metallics [23] also revealed a reduced value of the ground state 4f moment.

Similarly in NdCo_5 [24], the Nd moment at 4.2K is $2.8 \mu_B$ instead of $3.27 \mu_B$ for the saturated ion giving evidence for a ground state which results from mixing between different $|JM\rangle$ states.

Fig. 6 : Holmium magnetic amplitudes in HoFe_2 (ref. 21, 22).

c) Exchange and CEF interactions

Exchange and CEF interactions acting on the rare-earth ions determine the 4f ground state. The exchange interactions are usually treated in the molecular field formalism as equivalent to a magnetic field :

$$\mathcal{H}_{\text{ex}} = -g_J \mu_B \vec{H}_{\text{ex}} \cdot \vec{J}$$

where $\mathcal{H}_{\text{ex}}$ is the exchange field. Using the Stevens operator formalism, the CEF interactions may be written as :

$$\mathcal{H}_{\text{CEF}} = B_{\ell}^m O_{\ell}^m$$

where the number of operators O_{ℓ}^m involved depends on the symmetry of the environment and the B_{ℓ}^m are considered as parameters.

In the $\text{RA}\ell_2$ compounds [25], cubic crystal field parameters were obtained by neutron spectroscopy in the paramagnetic state, and exchange interactions from magnetostatic measurements in the ordered state. The 4f ground state calculated by diagonalization of the total Hamiltonian, including CEF and exchange interactions, is, for example in NdAl_2 , in close agreement with the ground state corresponding to the measured form factor at 4.2K. This shows the CEF and exchange interactions to be correctly described in the above formalism. On the other hand, the compound HoAl_2 in order to account for the Ho ground state measured in the polarised neutron experiment (Fig.1f) [26] would need larger values of CEF parameters than deduced from neutron spectroscopy. Such a discrepancy suggests that higher-order terms are involved in the exchange interactions. Similar behaviour is known to occur in RZn [27] alloys. The Tm form factor in TmZn [28] was interpreted by considering quadrupolar pair interactions :

$$\mathcal{H}_Q = -G_1 \langle O_2^0 \rangle O_2^0$$

then, magnetization measurements in the ordered state, spin wave excitations and Tm form factor could be accounted for by considering a unique set of CEF and exchange interactions [29].

As already described there are cases where the ground state is not $|JJ\rangle$ even when exchange interactions largely overcome CEF interaction. To account for the moment reduction in HoFe_2 [21,22] and NdCo_5 [24] would need in the molecular field formalism huge values of CEF parameter, which is unrealistic. Although it has always been assumed that the molecular field model is an excellent approximation for interpreting magnetic properties, especially when large 4f-3d interactions are involved, the results of form factor measurements show that as far as the rare earth ground state is concerned such an approximation is not valid. Here also higher order terms are involved in exchange interactions; but in HoFe_2 and NdCo_5 , the exchange interactions involve 3d electrons for which the orbital contribution to the magnetization is small. Then biquadratic spin interactions are very unlikely to be so large. But the magnetic interactions occur through the conduction band, and similar properties may be due to a failure of the RKKY theory when the band magnetization is large. The magnetic properties of the compound GdMg [29], the magnetic structure of which is canted [30], can be quantitatively understood when introducing biquadratic pair interactions phenomenologically [31].

5. Polarization of the conduction electrons

a) Evidence for a conduction electron polarization

In most of the above cases, where the experimental magnetic amplitudes have been compared to those calculated for a 4f electron configuration, a significant discrepancy was present for the low angle reflections. This shows that there exists in the cell a magnetization density which has not a 4f character and particularly, which is not as localized around the nuclei. This is also apparent in real space where some magnetization density, far from the Nd nuclei, can be seen, as, for example, in the projection along the [001] axis of NdAl_2 (Fig. 7a).

Fig. 7 : Projection of the magnetization density ($\mu_B/\text{\AA}^2$) for different rare earth Laves phases a) total density in NdAl_2 , extra density in b) NdAl_2 , c) CeAl_2 , d) HoFe_2 .

One can then consider the existence of 2 contributions to the magnetic amplitudes : one due to the 4f electrons and another one resulting from the polarization of the conduction electrons. It is possible however to separate these 2 contributions without making any assumption on the exact shape of the 4f electron form factor. Such a separation initiated by MOON et al. in metallic Gd [6], is based on the different localizations expected for the 2 types of magnetization : a distinction can be made between a first magnetization $m_{\text{loc}}(\vec{r})$, very localized around the rare earth nuclei, and a second magnetization $m_{\text{extra}}(\vec{r})$, more diffuse :

$$m(\vec{r}) = m_{\text{loc}}(\vec{r}) + m_{\text{extra}}(\vec{r})$$

Consequently the magnetic structure factors are the sum of 2 magnetic contributions :

$$F_M = F_{M_{\text{loc}}} + F_{M_{\text{extra}}}$$

where $F_{M_{\text{extra}}}$ is assumed to vanish very rapidly with $\sin \theta/\lambda$ due to the poor localization of $m_{\text{extra}}(\vec{r})$. The $F_{M_{\text{loc}}}$ contributions to the first Bragg reflections are determined as those which give a magnetization density $m_{\text{loc}}(\vec{r})$, as close to zero as possible between the rare earth atoms.

Table II displays the values of $F_{M_{\text{loc}}}$ determined for the first Bragg reflections of NdAl_2 , and compares them with the structure factors $F_{M_{4f}}$ calculated by considering the 4f electron contribution only and the wave function as determined previously (section 4.b). The two methods, the first based on the localization criterion only, and the second assuming the knowledge of the 4f form factor, give very similar results.

hkl	$F_{M_{\text{obs}}}$	$F_{M_{\text{loc}}}$	$F_{M_{4f}}$
0 0 0	2.470(20)	2.629(35)	2.608
2 2 0	2.401(19)	2.445(24)	2.449
4 0 0	2.192(25)	2.282(15)	2.294
4 4 0	1.997(28)	1.973(6)	1.991

Table II : Comparison of the magnetic structure factors of the first Bragg reflections for NdAl_2 : observed structure factor $F_{M_{\text{obs}}}$, localized structure factors $F_{M_{\text{loc}}}$ and 4f electron structure factor $F_{M_{4f}}$ calculated for $|\psi_{\text{Nd}}| > 0.88$ | $9/2 > + 0.45$ | $1/2 > - 0.11$ | $- 7/2 >$.

The conduction electron contributions are then obtained by simple subtraction. In the case of NdAl_2 these contributions become very small above $\sin \theta/\lambda = 0.35 \text{ \AA}^{-1}$.

b) Which electrons contribute to the extra magnetization

The conduction electron magnetization density $m_{\text{extra}}(\vec{r})$ is obtained by a simple Fourier transform of the structure factors : $F_{M_{\text{extra}}}$. This density is represented in Figure 7 for 3 compounds having the same crystal structure : NdAl_2 , CeAl_2 and

HoFe_2 . In the case of NdAl_2 , it is also compared to the total magnetization density. As expected, some density $m_{\text{extra}}(\vec{r})$ is present far from the rare earth nuclei. This localization is far less than that of the 4f moment as seen in figures 7a and 7b.

The spatial extension of the extra magnetization density is very similar for the different compounds. For the 3 compounds of figure 7, it is striking. This implies that for the different compounds, the same electronic shell is polarized by the 4f moment. One can then compare this magnetization density to that resulting from atomic calculations, and particularly to that of the 5d shell. However the 5d electrons are very sensitive to the ionicity of the rare earth atom : according to Desclaux [32], the 5d electrons are almost free in the neutral atom R^0 while in the tripositive ion R^{3+} they are fairly localized. The experimental 5d form factor is intermediate between these 2 extreme cases (Figure 8). It is therefore possible to consider the conduction electrons which are polarized by the 4f moments as essentially atomic 5d electrons. But, for these electrons, the extra potential resulting from the ionization of the rare earth atom is partially screened.

Figure 8 : 5d magnetic amplitudes for HoAl_2 measured at 4.2K and calculated for Ho^0 and Ho^{3+} (ref. 22, 32).

3) Sign and magnitude of the 5d polarization

In all the cases of rare-earth metals or rare-earth compounds where the magnetization density has been investigated, with the sole exception of cerium compounds, the magnetization of the conduction electrons is parallel to the spin S of the 4f shell. It results in a negative magnetization for the first half of the rare-earth where $J = L-S$, and a positive magnetization for the second half where $J=L+S$. This underlines the role of the 4f spin as a driving force to polarize the conduction electrons and suggests to scale the 5d magnetization to the spin : $M_{5d} = \alpha < S_z >$. As this simple law does not fit the experimental data, it has been proposed by BELORIZSKY, NIEZ and LEVY [33] to include the 4f orbit in the driving mechanism : $M_{5d} = \alpha < S_z > + \beta < L_z >$. Table III shows that satisfactory agreement can be obtained for the RAl_2 series.

	M_{total}	M_{4f}	$\langle S_z \rangle$	$\langle L_z \rangle$	M_{5d}^{OBS}	$M_{5d}^{\text{cal}(\alpha, \beta)}$
NdAl_2	2.45	2.61	- 1.20	5.00	- 0.16	- 0.13
SmAl_2	0.23	0.53	- 1.61	3.73	- 0.30	- 0.26
GdAl_2	7.25	6.60	3.30	0	0.65	0.76
HoAl_2	9.29	8.63	1.73	5.17	0.66	0.55

Table III : Magnitude of the conduction electron polarization (μ_B).

Figure 9 : Magnetic amplitude measured at different temperatures in CeSn_3 (ref.35).

The situation is reversed in cerium compounds where the 5d magnetization is parallel to the 4f moment although $J = L-S$. In this case, the exchange mechanism with conduction electrons is different. Schrieffer and Wolf [34] have shown that besides the normal contact interaction which is positive for all the rare-earth atoms, there exists for cerium a resonant exchange, negative and larger than the normal exchange. This negative exchange, which explains resistivity anomalies and Kondo behaviour in cerium compounds, is directly confirmed by neutron diffraction.

In addition, the different values of the 5d polarization are associated with different behaviour, observed in several cerium compounds. For instance, in the Kondo system CeAl_2 , the 5d polarization represents 20 % of the 4f moment. On the other hand, at low temperature in CeSn_3 [35], the 5d polarization is equal to the 4f moment (Figure 9), which confirmed the mixed valence character of this compound. However, this polarization decreases at higher temperatures and above 40K it has practically disappeared. Such a thermal variation is not fully understood for the moment. Other studies of these phenomena should help for the understanding of the complex magnetic properties in both Kondo and mixed valence systems.

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