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Influence of interface effects on a rare-earth crystal field in iron–rare-earth multilayers

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Mössbauer spectroscopy and magnetization measurements (mean and high field) were carried out on Fe-R multilayers, where R =Nd and Tm. From the high-field (20-T) magnetization measurements, the magnetic moment of 3.27 μ_B/at. for neodymium was found. It is the first experimental evidence of the free-ion magnetic moment for Nd metal in multilayers. Perpendicular and in-plane anisotropy directions for NdFe and TmFe multilayers, respectively, were observed. An original explanation of these phenomena, taking into account modifications of the rare-earth crystal field due to the layered structure and artificial periodicity, is proposed.

INTRODUCTION

Thin-film multilayers have recently gained considerable scientific and technical attention. Compositional modulation allows one to manufacture the film composed of a few-Å thick layers of different elements which results in an artificial structure. The imposed periodicity significantly modifies the electronic and magnetic properties.[1] In this respect it seems interesting to study the magnetism and interface effects in T-R (transition-metal–rare-earth) compositionally modulated structures in order to see if and how the magnetic coupling and anisotropy mechanisms are differentiated from those in classical bulk materials. Recent studies of magnetic multilayers have been focused on the propagation of magnetic ordering through the artificial periodicity.[2] Our idea was to use a many-interface system in order to create an artificial crystal field and modify the magnetic properties in respect to pure elements and alloyed thin films.

We have chosen two iron–rare-earth systems with rare-earth elements from the opposite sides of the rare-earth series (light and heavy rare-earth) with a different electric charge distribution, and its consequences are evidenced in Fe-R crystalline compounds.[3] In T-R compounds, the magnetic ordering is mostly dominated by the strong T-T exchange interactions, while the magnetic anisotropy at low temperatures arises from rare-earth ions in the crystal field. For Fe-R compounds, when R is a light rare earth (less than half the $4f$ shell is full and $J=L-S$), ferromagnetic $3d$-$4f$ exchange interactions are found. On the contrary, when R is a heavy rare earth (more than half the $4f$ shell is full and $J=L+S$) antiferromagnetic coupling with the Fe moment exists.[3] The interplay of the Fe-R exchange field and the crystal electric field acting on rare-earth ions in these compounds has an essential effect on a magnetic property such as anisotropy. The crystal-field-induced anisotropy arises as a consequence of the interaction between the electrostatic field of the ions surrounding the rare-earth site and an asymmetric charge cloud of the $4f$ electrons. This charge cloud may have a cigarlike (as it is for Tm) or a pancakelike shape (as it is for Nd). The difference in shape is reflected in the sign of the second-order Stevens's factor denoted as α_j (following the notation used by Hutchings[4]), which is positive for cigarlike and negative for pancakelike shapes of the $4f$ orbital. The resulting easy magnetization direction is perpendicular ($\alpha_J<0$) or parallel ($\alpha_J>0$) to the c axis for Nd and Tm, respectively. We report here the results of Mössbauer spectroscopy and magnetization measurements (mean and high field) of Fe-Nd and Fe-Tm multilayers.

EXPERIMENTAL

The samples were prepared by the alternate evaporation of the rare-earth and Fe layers in an ultra-high-vacuum chamber (10^{-10} Torr) onto a substrate held at 410 K, which was the optimal temperature in respect to minimizing the interface roughness. Characterization of the samples regarding periodicity, interfaces quality, and atomic structure was made by means of x-ray diffraction, electron microscopy, and resistivity measurements. All films were continuous and microcrystalline. Crystal dimensions depend on the layer thickness in the sample, and vary between 200 and 300 Å and 50 and 100 Å for iron and rare-earth ions, respectively. The rare-earth layer thickness was kept constant: 38 Å for Nd and 36 Å for Tm, while the Fe layer thickness was varied between 13 and 31 Å. The total thickness of each sample was about 1 μm.

Mössbauer spectroscopy and magnetization measurements, using a vibrating-sample magnetometer (VSM) with $H\leq 2$ T, were carried out on R-Fe multilayers. High-field experiments (up to 20 T) were performed at the Service National des Champs Intenses (SNCI) in Grenoble.

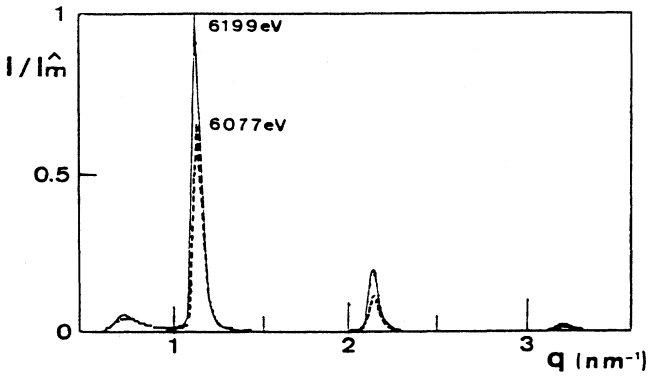

FIG. 1. The rocking curves of the 16 Å/37 Å Fe-Nd multilayer sample recorded near the L_{III} edge.

RESULTS AND DISCUSSION

X-ray diffraction in a multilayer structure is determined by the electronic concentration profile, which depends both on the atomic concentration and the specific volume. Probing with photons of different wavelengths in the vicinity of an absorption edge (anomalous x-ray scattering) produces a variation of the scattered intensity which allows a separation of both contributions. Measurements of several multilayer systems were performed (for details see Ref. 5). Here we present a typical θ-2θ scan measured at 6199 and 6077 eV for Fe-Nd multilayer. Three satellites were usually observed, with shape and q position independent of photon energy. Three peaks clearly visible in Fig. 1 prove good periodicity and sharp interfaces.

Figure 2 shows the Mössbauer spectra for two Nd-Fe samples: 38 Å/13 Å and 38 Å/31 Å of Nd-Fe layer thicknesses at $T=4.2$ K and $H=0$. The corresponding spectra of Tm-Fe multilayers are shown in Fig. 3 (also at $T=4.2$ K and $H=0$). From the Mössbauer spectra the easy magnetization direction can be determined. For the Nd-Fe samples it is perpendicular to the film plane (3:0:1 peak intensity); however, the appearance of the small second peak (visible for the sample with 31 Å Fe) signifies some tendency of the easy direction to leave this axis—angle $\theta=11°$ was estimated by a computer fit. For the

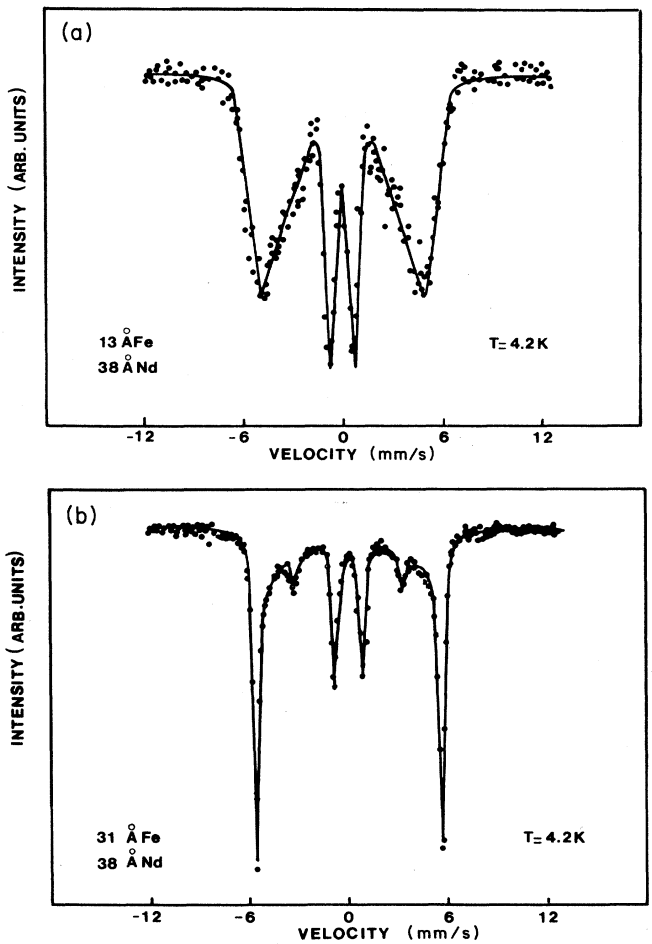

FIG. 2. The Mössbauer spectra of Nd-Fe multilayers at $T=4.2$ K and $H=0$, for the samples with an Fe layer thickness of 13 and 31 Å.

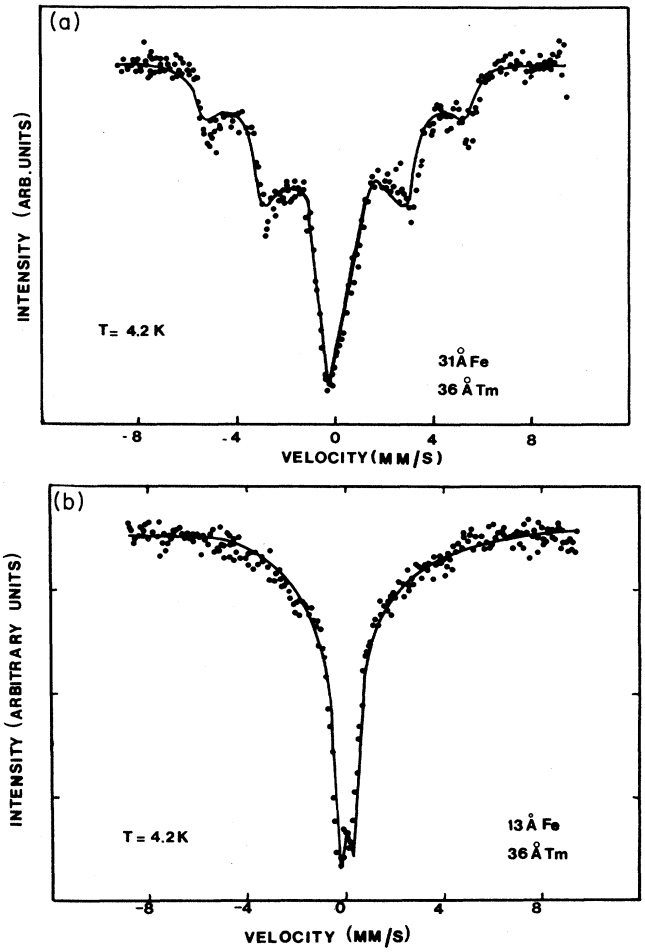

FIG. 3. The Mössbauer spectra of Tm-Fe multilayers at $T=4.2$ K and $H=0$, for the samples with an Fe layer thickness of 13 and 31 Å.

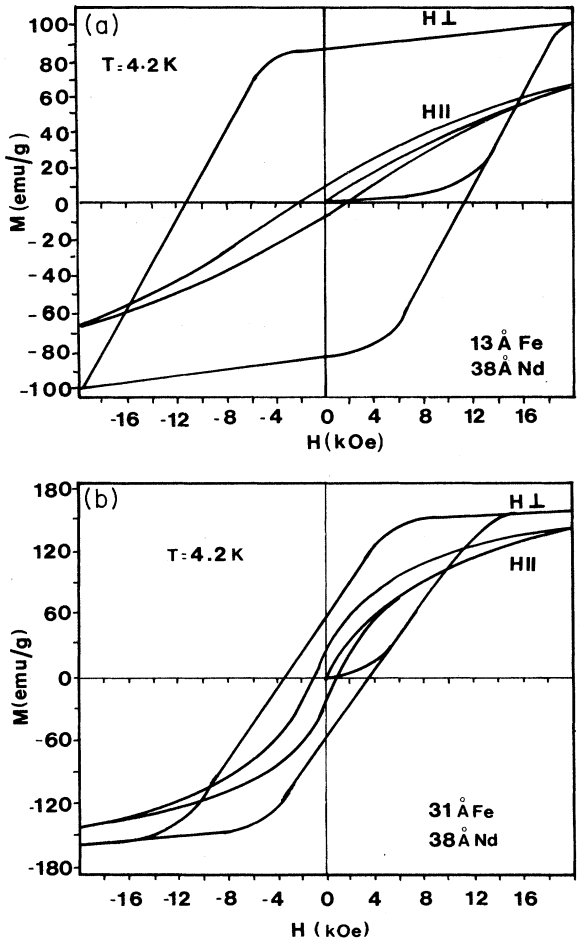

FIG. 4. Hysteresis loops of Nd-Fe multilayers at $T=4.2$ K for the samples with an Fe layer thickness of 13 and 31 Å, and two different applied field directions.

Tm-Fe system the best computer fit with the experimental data was obtained for the easy axis in the sample plane. The spectra were fitted with the hyperfine field distribution, and the relative peak intensity was determined by a least-square method. The anisotropy results were fully corroborated by the magnetization measurements. From the ^{57}Fe hyperfine field distribution two magnetic sites of Fe in Nd-Fe multilayers were determined. One corresponds to the pure Fe layer and the second probably corresponds to the iron atoms situated at the interfaces where an Nd-Fe alloy is formed. About 40% of the Fe atoms are located at the interfaces for the sample with 31 Å of Fe layer thickness, which results in about a 6-Å interface thickness from each side of the iron layer. For the Tm-Fe system, the existence of a quadrupolar effect can be clearly seen. Nonmagnetic Fe site ratios were estimated at 60% in the 36 Å/13 Å Tm-Fe sample and 30% in the 36 Å/31 Å Tm-Fe sample.

On the basis of the ^{57}Fe hyperfine field distribution, a mean magnetic Fe moment was calculated using the usual conversion of 145 kOe/μ_B.[6] For the Nd-Fe system, $\mu_{Fe}=1.74$ and 2.1 μ_B/at. were found for an Fe layer thickness of 13 Å and 31 Å, respectively. In the Tm-Fe multilayers (after subtracting the quadrupolar effect contribution), the corresponding Fe moments were 0.57 and 1.15 μ_B/at. Mössbauer spectroscopy measurements under the external magnetic field of 6 T were also carried out for the Nd-Fe multilayers. The induced magnetic moment of 0.12 μB/at. Fe was found for the 38 Å/13 Å Nd-Fe sample.

The magnetic field dependence of the magnetization $M(H)$ for a direction of the applied field parallel and perpendicular to the film plane was measured within the temperature range of 4.2–300 K. For all Nd-Fe samples, strong perpendicular anisotropy was found at 4.2 K, which can be seen in Fig. 4, where hysteresis loops for two Nd-Fe samples are shown (38 Å/13 Å and 38 Å/31 Å Nd-Fe). High-field data at $T=4.2$ K for the 38 Å/13 Å Nd-Fe sample are presented in Fig. 5.

For the Tm-Fe system in-plane anisotropy was observed (see Fig. 6). Those are the first results reported on Tm-Fe multilayers, but for Nd-Fe some were already published. Hosoito *et al.*[7] found easy axis perpendicular to the film plane, while Sellmyer *et al.*[8] reported that no clear evidence for perpendicular anisotropy has been observed. The latter result is highly surprising because it is contrary to the results of Shinjo[7] and the present paper on multilayers and moreover with all previously reported results concerning the Nd-Fe system either amorphous or crystalline, in the form of thin films or melt-spun ribbons[9–11] where perpendicular anisotropy was always found. The interface effects considered in this paper as a main source of anisotropy in multilayers are distance dependent and could explain, perhaps, Sellmyer's observation for the samples with thick (100 Å) layers.

As in Fe-R compounds, ferromagnetic coupling of $3d$-$4f$ moments in Nd-Fe and antiferromagnetic coupling in Tm-Fe multilayers were found. From the magnetiza-

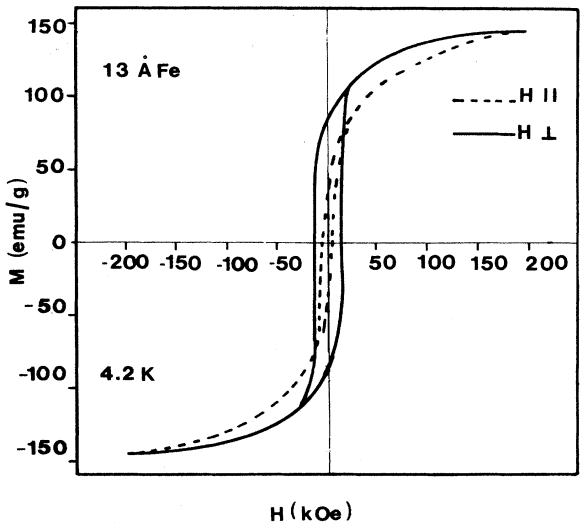

FIG. 5. High-field (20-T) magnetization loops for the 38 Å/13 Å Nd-Fe sample at 4.2 K, and two different applied field directions.

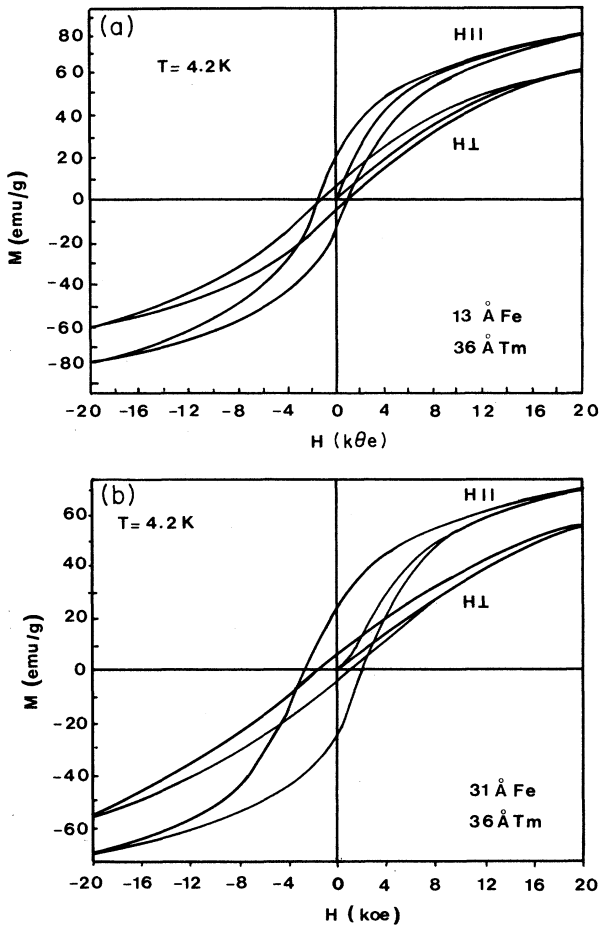

FIG. 6. Hysteresis loops of Tm-Fe multilayers at $T=4.2$ K for the samples with an Fe layer thickness of 13 and 31 Å, and two different applied field directions.

tion values at $H=2$ T measured along the easy axis, and mean Fe moments obtained from Mössbauer spectroscopy, the magnetic moments of Nd and Tm were calculated in Nd-Fe and Tm-Fe multilayer systems. The results are summarized in Table I.

Additional results were obtained from high-field (20 T) measurements. Saturation-magnetization (saturation magnetic moment) values for the measured samples were found, and on their basis rare-earth magnetic moments were calculated for each sample using the iron moment obtained from Mössbauer spectroscopy plus a high-field-induced moment of 0.12 μ_B/at. Fe. The value close to the free-ion magnetic moment for Tm (7 μ_B/at.) is not a surprise, because, as is well known,[12] even the field of 3 T along the easy axis is sufficient to produce a ferromagnetic structure with free-ion moments. However, the situation is totally different for Nd, where at $H=34$ T the moment is only 2.23 μ_B/at.,[13] still well below the free-ion value of 3.27 μ_B/at. The first experimental evidence of the free-ion value of the magnetic moment for the Nd metal was obtained from magnetization measurements of Nd-Fe multilayers at $T=4.2$ K and $H=20$ T. For 38 Å/13 Å and 38 Å/31 Å Nd-Fe samples, Fe magnetic moments of 1.86 and 2.2 μ_B/at. (with the induced moment correction of 0.12 μ_B/at.) were used, respectively, which resulted in neodymium moments of 3.28 and 3.30 μ_B/at., corresponding exactly to the free-ion value (within the experimental error of ± 0.1 μ_B/at.).

Obtained results give clear evidence that the magnetic behavior of thin Nd layers in a multilayered structure is quite different than that of bulk Nd metal. We believe that the main reason for this is the influence of the interfaces on the Nd crystal field in the compositionally modulated structure. Of course one should be aware of the strong exchange coupling between $3d$ and $4f$ moments, which increases the effective magnetic field. The main role of this magnetic coupling via the conduction electrons in the Ruderman-Kittel-Kasuya-Yosida (RKKY) relatively long-range interaction is to align the $3d$-T moment with the $4f$ moment of the rare-earth in the Fe-R multilayers. Strong exchange coupling alone is not a sufficient factor to get a free-ion Nd moment, as can be seen from magnetic measurements on NdFe compounds[3] or crystalline and amorphous NdFe thin films,[9-11] where for the corresponding compositions even at $H=2$ T the Nd is significantly lower than that obtained in the Nd-Fe multilayers at the same external field. In order to give an idea of the importance of interface effects, we have calculated crystal-field intensity parameters on the basis of a point-charge model assuming ideal, sharp interfaces.

The most general Hamiltonian for a hexagonal crystal field can be written[14]

$$\mathcal{H}=B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6 , \quad (1)$$

where B_n^m are crystal-field intensity parameters and O_n^m represent operators, which are well-known polynomials in the angular momentum operators. They are tabulated by Hutchings[4] for various values of J. In fact, for a cubic symmetry and also for hexagonal structure with the per-

TABLE I. Magnetization (m) and magnetic moment (μ) of Nd-Fe and Tm-Fe multilayers at $H=2$ T.

Sample Thickness (Å)/(Å)	m (emu/g)	μ (μ_B/at.)	μ_{Fe} (μ_B/at.)	μ_{Nd} (μ_B/at.)	μ_{Tm} (μ_B/at.)
NdFe 38/13	107.1	1.92	1.74	2.1±0.1	
NdFe 38/31	160.3	2.34	2.1	2.9±0.1	
TmFe 36/13	78.2	1.59	−0.57		3.7±0.1
TmFe 36/31	68.1	1.11	−1.15		6.6±0.1

fect packing ratio $c/a=2\sqrt{2}/3=1.63$, the second-order term B_2^0 in Eq. (1) vanishes.[14] For Nd and Tm metals this ratio is very close to the ideal value and as a result one can assume $B_2^0=0$ (the real value of the parameter, $B_2^0=0.08$ cm^{-1}, was deduced from neutron inelastic scattering measurements on double hcp Nd by Stanley and McEwen[15]). Thus in this special case of the hexagonal structure, the dominant term is B_4^0 and the fourth-order Stevens factor β_J determines the anisotropy direction. For Nd, β_J and α_J are negative, whereas for Tm, β_J and α_J are positive, which results in a different easy axis direction for each element ($\perp c$ and $\| c$, respectively). Lehmann-Szweykowska[16] has considered the symmetry restrictions imposed on possible splittings of the $J=\frac{9}{2}$ multiplet by Eq. (1). The author further categorized level schemes by giving ground-state wave functions. Estimations of the energy levels, based on the point-charge model with an antishielding correction, suggested an overall splitting of less than 200 K on both types of sites (cubic and hexagonal), and are consistent with the interpretation of Lebech *et al.*[17] As was shown by Lehmann-Szweykowska, the dominant components of Nd ground-level wave functions are the following states: $|\frac{9}{2};\frac{5}{2}\rangle$ and $|\frac{9}{2};\frac{7}{2}\rangle$, with a small contribution of $|\frac{9}{2};\frac{1}{2}\rangle$ for cubic sites. In the compositionally modulated structure with artificial periodicity, the crystal-field Hamiltonian is modified due to the presence of interfaces. The symmetry of the bulk Nd is changed significantly by the presence of a well-defined symmetry axis perpendicular to the film plane in the multilayered structure, and a nonzero second-order term B_2^0 appears in the Hamiltonian. The new term (H_{if}) in the crystal-field Hamiltonian resulting from the interface effect can be described in the uniaxial model as

$$H_{if}=B_2^0 O_2^0=B_2^0[3J_z^2-J(J+1)] , \tag{2}$$

where J_Z is the angular momentum projection along the new symmetry axis z, which is perpendicular to the film plane in the multilayered structure. Appearance of the strong B_2^0 term results in different crystal-field level splittings and different crystalline effective field (CEF) ground-state wave functions. Assuming the charge (0) of Fe atoms (due to conduction-electron shielding) and sharp interfaces between Fe^0 and Nd^{3+} (Tm^{3+}), we have calculated the value of B_2^0 on the basis of a point-charge model:

$$B_2^0=A_2^0\langle r^2\rangle\alpha_J , \tag{3}$$

$$A_2^0=-|e|\gamma_{20}\tfrac{1}{4}\sqrt{5/\pi} , \tag{4}$$

$$\gamma_{20}=\sum_j \frac{4\pi}{5q_j}\frac{Z_{20}(\theta_j,\phi_j)}{R_j^3} , \tag{5}$$

where a_j is a charge of the j atom, R_j, θ_j, and ϕ_j are spherical coordinates of the j atom, Z_{nm} are the usual tesseral harmonics (see Ref. 4). Using the preceding equations we have obtained $B_2^0=-17.4$ cm^{-1} for Nd and $B_2^0=21.5$ cm^{-1} for Tm. Using the Fe charge value (-0.5), as proposed by some authors, B_2^0 becomes even more important; -24 and 32 cm^{-1} for Nd and Tm, respectively. Indeed, this term is much larger in comparison to the terms $B_4^0=0.06$ cm^{-1}, $B_6^0=-0.03$ cm^{-1}, and $B_6^6=0.0019$ cm^{-1} present in the CEF Hamiltonian for bulk Nd metals, calculated by Lehmann-Szweykowska,[16] and the terms $B_2^0=0.08$ cm^{-1}, $B_4^0=0.01$ cm^{-1}, $B_6^0=0.0007$ cm^{-1} obtained by McEwen.[15] On the other hand, the obtained value of B_2^0 is comparable to $B_2^0=-4.3$ cm^{-1} obtained by Buschow *et al.*[18] from Mössbauer measurements for the $Nd_2Fe_{14}B$ compound. Moreover, in the layerlike structure of $Nd_2Fe_{14}B$, magnetic moment of Nd (3.2) μ_B/at. very close to the free-ion value was obtained from high-field magnetization measurements by Verhoef *et al.*[19]

As was already shown, the interface contribution term in the CEF Hamiltonian is dominant, so the higher-order terms can be neglected in a first approximation. As eigenfunctions of J_z diagonalize the Hamiltonian H_{if} [Eq. (2)], the crystal-field energy levels can be simply obtained from the value of B_2^0, and the high moment state $|\frac{9}{2};\frac{9}{2}\rangle$ prevails in the ground-state level. The other states present in the fundamental level due to small higher-order CEF intensity parameters B_4^0, B_6^0, and B_6^6 are much less important, becoming negligible at high magnetic fields. This can explain why the free-ion moment was reached for Nd in a multilayered structure at $H=20$ T. The same procedure was used for thulium, and in this case the state $|6;0\rangle$ is a dominant one in the ground-state level.

The proposed model explains as well the experimental results concerning anisotropy directions for both systems studied in this work—perpendicular for Nd-Fe and in plane for Tm-Fe multilayers. The uniaxial crystal field along the symmetry axis z defined in Eq. (2), created in multilayered structures, determines the anisotropy direction. For Nd the high moment state $|\frac{9}{2};\frac{9}{2}\rangle$ contributes mainly to the CEF fundamental level, and the z axis becomes the easy magnetization direction—perpendicular to the film plane. For thulium the low moment state $|6;\dot{0}\rangle$ constitutes the fundamental CEF level and the z axis is the hard magnetic direction.

One can conclude that for R-T multilayers, where A_2^0 was found to be positive and the B_2^0 term is nonzero due to the uniaxial crystal field, the sign of the second-order Stevens's factor (α_J) is essential for the anisotropy direction. For rare-earth ions with $\alpha_J<0$, perpendicular anisotropy can be expected, and, on the other hand, for rare-earth ions with $\alpha_J>0$ one can predict in-plane anisotropy. Indeed, this is fully confirmed by the experimental data. The results published for Tb-Fe (Ref. 20) and Dy-Fe (Ref. 21) multilayers are in full agreement with the proposed model. Tb and Dy have α_J negative (like Nd), and perpendicular anisotropy was found in both cases. Moreover, our recent results on Er-Fe multilayers[22] (Er has $\alpha_J>0$) fully confirmed the aforementioned prediction, and in-plane anisotropy was observed.

One more conclusion can be arrived at from the presented results. It is not possible to consider the anisotropic pair ordering with associated magnetic dipolar interactions as a main source of anisotropy in T-R multilayers, as was proposed by many authors recently. In this

model the basic idea is that creating an artificially structured material of $ABAB$ form, there is an excess of AB pairs along the direction perpendicular to the film's plane. However, the formation probability of such atomic pairs is certainly equal for Tb as for Tm (and other rare-earth ions), so following this model one should obtain perpendicular anisotropy for all R-Fe multilayers, which is in contrast with presented experimental results.

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