

^{151}Eu Mössbauer study of transition-metal/Eu multilayers

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(Received 14 July 1995)

The magnetic properties of TM/Eu (TM=V, Cr, Fe, Co, Ni, Cu, and Nb) multilayers have been studied by ^{57}Fe and ^{151}Eu Mössbauer measurements at 4.2 and 300 K. The ^{57}Fe Mössbauer spectra at 4.2 and 300 K of the Fe/Eu multilayers were fitted with two components: one with hyperfine parameters typical of bulk α -Fe, and the other one with a reduced magnetic hyperfine field, which is attributed to the interface region. The ^{151}Eu Mössbauer spectra of TM/Eu at 4.2 K were similarly analyzed with two components: component *A* with hyperfine parameters similar to bulk Eu metal, and component *B* with a reduced magnetic hyperfine field. Variation of the Eu layer thickness for the systems Fe/Eu and V/Eu showed an enhancement of component *B* relative to component *A* with decreasing Eu layer thickness, supporting the analysis with two components given above. The latter component is attributed to the interface region. Possible explanations for the reduction of the magnetic hyperfine field of component *B* are discussed.

I. INTRODUCTION

Metallic multilayers in the form of thin films composed of alternating stacking of different metals have shown fascinating magnetic properties which depend on layer thicknesses due to the magnetic coupling through the layers^{1,2} and magnetic properties related to magnetic coupling at the interfaces.³ Multilayers of *3d* (Fe) and *4f* rare-earth (*R*=Pr, Nd, Tb, and Dy) metals are interesting because Fe spin reorientation is observed as a function of temperature.⁴

In this paper we present the magnetic properties at the interfaces of Eu layers sandwiched between different types of magnetic (Cr, Fe, Co, and Ni) and nonmagnetic (V, Cu, and Nb) transition metals (TM). Eu metal in the bulk has *4f* electronic configuration of divalent Eu, with an antiferromagnetic helical spin structure below 90 K and a little magnetic anisotropy. The *3d* TM elements, except Fe, Ni, and Cu, do not form solid solutions or intermetallic compounds with Eu in the equilibrium state.

We used ^{57}Fe and ^{151}Eu Mössbauer measurements to study the local magnetic properties of the interface region in the multilayers. For the study of Fe/Eu multilayers, it is a great advantage that both components, Fe and Eu, include Mössbauer probes.

II. EXPERIMENT

The Eu based multilayers were prepared by alternate deposition in ultrahigh vacuum (about 10^{-9} mbar). The films were deposited onto polyimide substrates kept at -50°C . In this work, the TM layer thickness was fixed at 40 Å for all multilayers, while the Eu layer was held at 30 Å. Only in the case of Fe/Eu and V/Eu multilayers, the Eu thickness varied between 3000 and 30 Å. Because Eu is one of the most reactive *R* metals, the deposition started and finished with a *TM* layer. Finally a Cr or Au protection layer was put on the top of the film. X-ray-diffraction measurements were made

at low angle to confirm the artificial periodic structure of these multilayers and at high angle to check some preferential structural orientation and/or structural phase transition.

^{151}Eu and ^{57}Fe Mössbauer spectra were measured with a $^{151}\text{SmF}_3$ and a $^{57}\text{Co}:\text{Rh}$ source, respectively, by a conventional transmission geometry with the γ rays perpendicular to the film plane. The ^{151}Eu and ^{57}Fe spectra were taken at 300 and 4.2 K with the source and the absorber at the same temperature. The center shifts (CS) of ^{151}Eu Mössbauer spectra are given relative to the $^{151}\text{SmF}_3$ source, while the CS of ^{57}Fe Mössbauer spectra are given relative to α -Fe at RT. The absorbers were prepared by the superposition of several films in order to reach a Eu thickness of about 3000 Å to produce an acceptable signal-to-noise ratio. Even in these conditions the time necessary to obtain each spectrum was about 50 h.

III. SAMPLE CHARACTERIZATION

The x-ray-diffraction patterns in low and high angles for all the films are shown in Figs. 1(a) and 1(b), respectively. All samples have an artificial periodic structure with a periodicity of 70 Å resulting in the first, second, and third peaks at about 1.4, 2.6, and 3.8° [Fig. 1(a)].

The TM layers (40 Å) have the bulk polycrystalline structure with (110) bcc main peak for V, Cr, Fe, and Nb and (111) fcc main peak for Ni and Cu, between 38° and 45° as indicated in Fig. 1(b). Additional peaks with lower intensity are also observed in the diffraction patterns [see Fig. 1(b)]. Co layers show a peak at 76° , which is attributed to hcp (110) or fcc (220). Since the multilayers have been covered with a Cr layer, the corresponding Bragg peaks appear in the x-ray-diffraction patterns in Fig. 1(b).

The Eu layers have a bcc structure with (110) texture for most of the TM/Eu systems [Fig. 1(b)]. For Cr/Eu, Cu/Eu, and Ni/Eu multilayers, however, only a broad peak is observed around the Eu (110) peak position, indicating that the grain size of Eu in these layers is smaller compared to the

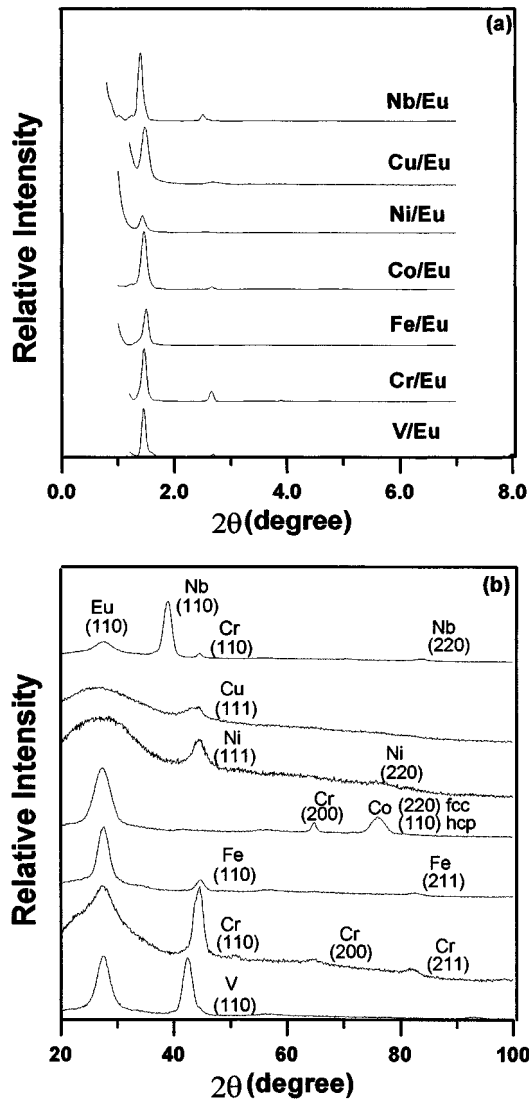


FIG. 1. (a), (b) X-ray-diffraction patterns in low and high angles for all samples of TM(40 Å)/Eu(30 Å) multilayers (TM=V, Cr, Fe, Co, Ni, Cu, and Nb).

other systems, with an even smaller grain size in the Cu/Eu and Ni/Eu multilayers compared to that in the Cr/Eu multilayer. The broadening of the peaks could also be an indication of an amorphous structure of the Eu layers or solid solution formation for Ni/Eu and Cu/Eu multilayers.

No oxide or hydride peaks appear in the x-ray-diffraction patterns for any of the samples taken just after the preparation. However, the Eu layers suffer gradual oxidation to EuO after some weeks. The samples used for Mössbauer measurements at 4.2 K suffer oxidation after few days due to some wetting in the He-bath cryostat through an aging process.

The in-plane magnetization curves taken up to 5 T for the Fe/Eu multilayer are roughly fitted by $M(H) = M_0 + \chi H$ at each temperature (Fig. 2). M_0 and χ are both temperature dependent. M_0 is due to the magnetization of the Fe layers and the antiferromagnetically exchange coupled interface region of the Eu layers; χ is the para(antiferro)magnetic contribution from the Eu magnetic moments in the inner part of the Eu layers.⁵

The ^{57}Fe Mössbauer spectra for Fe(30 Å)/Eu(40 Å)

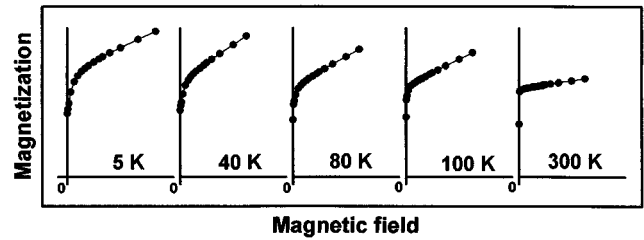


FIG. 2. Magnetization curves up to 5 T for Fe/Eu multilayer.

multilayer at 300 and 4.2 K are displayed in Fig. 3. They show that the Fe layers have two magnetic components: one with hyperfine parameters close to α -Fe and the other one with a reduced hyperfine field. This fitting model is consistent with a systematic study of ^{57}Fe Mössbauer spectroscopy in Fe/R multilayers reported by Mibu *et al.*⁴ From the ratio of two components and the assignment of the component with the reduced hyperfine field to the interface region (see below), we can conclude that the Fe thickness of the interface region for Fe/Eu multilayers is smaller than 3 Å, which shows that chemically sharp interfaces are realized in this system due to the immiscibility between Fe and Eu.

In another experiment, the coevaporation technique of Fe and Eu with *in situ* ^{57}Fe Mössbauer spectroscopy has been used to study the nonequilibrium alloy formation in the Fe/Eu system. We have observed the appearance of a paramagnetic component [$\text{CS}=0.24$ mm/s and QS (quadrupole splitting)=0.58 mm/s] which is not seen in our multilayer samples. The results, which support the absence of Fe/Eu alloying at the interfaces in our multilayer films, will be published elsewhere.⁶

IV. RESULTS

The ^{151}Eu Mössbauer spectra obtained at 300 K show that the Eu layers are not magnetically ordered, despite the fact that in case of the Fe/Eu multilayers, the Fe layers showed magnetic ordering at this temperature. The Eu magnetic mo-

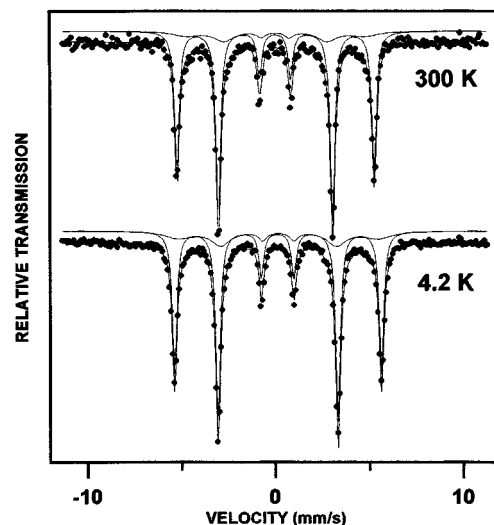


FIG. 3. ^{57}Fe Mössbauer spectra at 300 and 4.2 K for the Fe(40 Å)/Eu(30 Å) multilayers. (The full lines are obtained from least square method.)

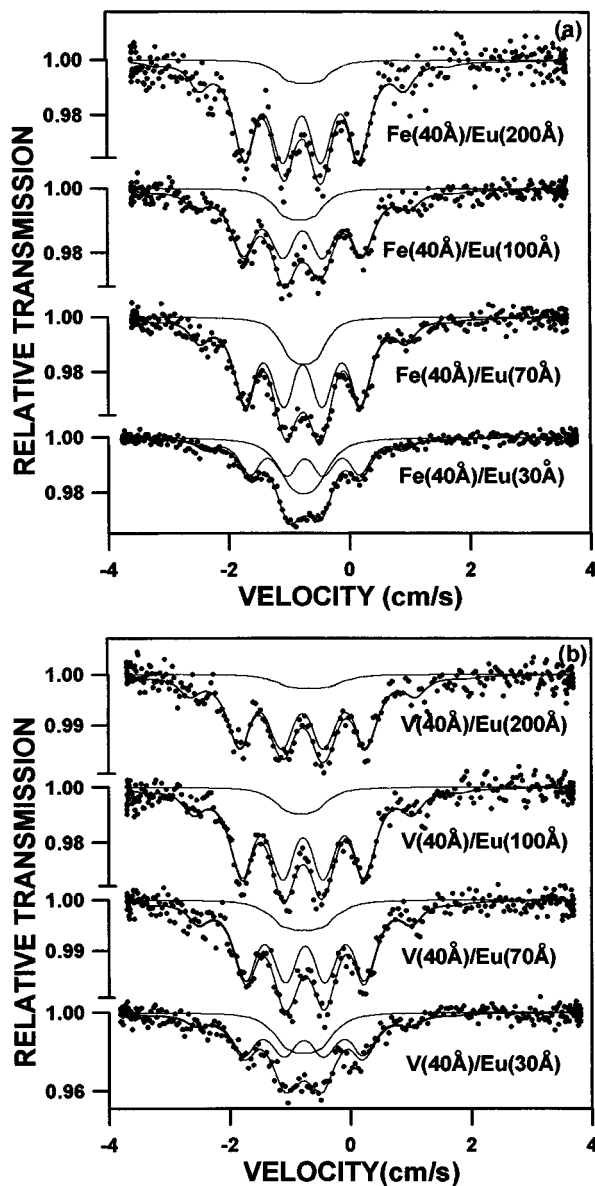


FIG. 4. (a), (b) ^{151}Eu Mössbauer spectra at 4.2 K for Fe(40 Å)/Eu(30 Å) and V(40 Å)/Eu(x Å) ($x=200, 100, 70,$ and 30 Å) multilayers as a function of Eu thickness. (The full lines are obtained from least square fits.)

ments at the interface region may be magnetically ordered through an exchange interaction with the Fe at the interface. However, the amount of this component seems to be too small to be detected by ^{151}Eu Mössbauer measurements at this temperature.

The ^{151}Eu Mössbauer isotope has a $7/2 \rightarrow 5/2$ nuclear transition which results in 18 Mössbauer transitions in the presence of a magnetic hyperfine field. Coincidence of some of these lines results in an 8-lines Mössbauer spectrum.

Figures 4(a) and 4(b) show the ^{151}Eu Mössbauer spectra of the Fe/Eu and V/Eu multilayers taken at 4.2 K which display a magnetic splitting. The symmetric shape of the spectra indicates the absence of Eu oxides and/or an electric field gradient at the ^{151}Eu sites.

The Mössbauer spectrum for the film with Eu layer thickness of 3000 Å is well analyzed using the Eu bulk hyperfine parameters. On the other hand, the spectra of Fe(40 Å)/Eu(x

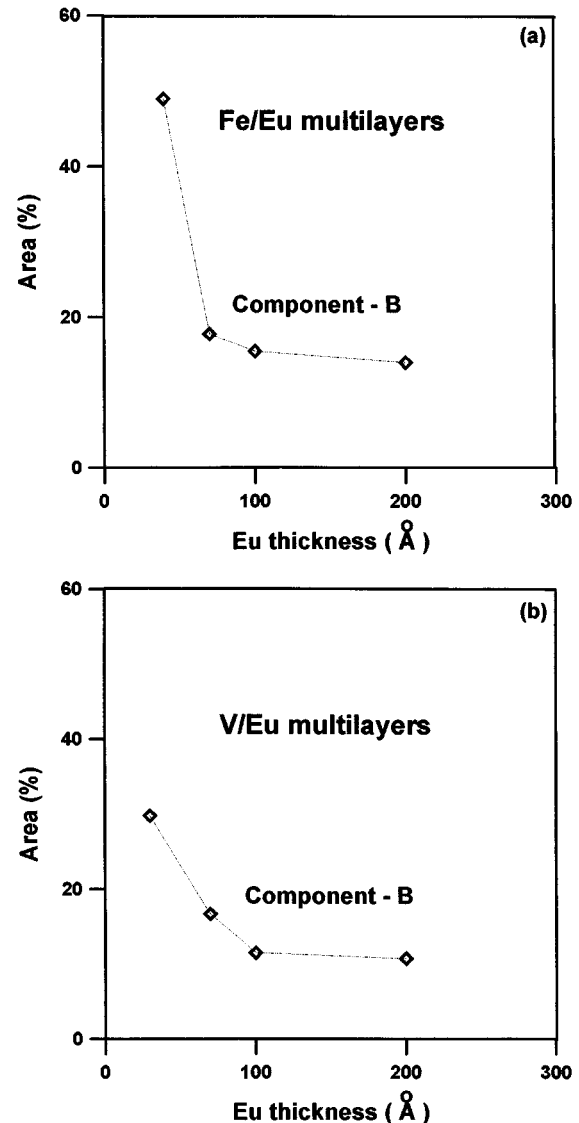


FIG. 5. (a), (b) Relative area (in %) of component B for Fe/Eu and V/Eu multilayers as a function of Eu thickness. (The full lines are only to guide the eyes.)

Å) and V(40 Å)/Eu(x Å) ($x=200, 100, 70,$ and 30) multilayers cannot be fitted using a single magnetic component. Therefore, based on the dependence of the Mössbauer spectra on the Eu layer thickness, we assume the coexistence of two magnetic components: one (component A) V/Eu, Cr/Eu, Fe/Eu, and Co/Eu multilayers can be fitted with two components (A and B). The spectra for the Ni/Eu and Cu/Eu multilayers have also been fitted with two components: one of them is the already known component B and the other one is a component C which is a single line around zero velocity [$\text{CS}=0.07(6)$ mm/s]. The latter component can be related to nonmagnetic Eu^{3+} , probably Eu^{3+} -oxide in an amorphous phase. However, due to the absence of any Eu^{+2} -oxide at the interface region (component B), we want to propose another interesting interpretation: Eu in small (amorphous) metallic particles may be in a nonmagnetic Eu^{3+} state. The argument of amorphous phase is supported by x-ray-diffraction patterns for these systems which show a broad line around the Eu (110) position as already mentioned above [see Fig. 1(b)]. For the Nb/Eu multilayer only a magnetically broad line is

TABLE I. Mössbauer hyperfine parameters at 4.2 K for all TM(40 Å)/Eu(x Å) multilayers with different types of TM, and with different Eu thickness. (A) corresponds to component A and (B) corresponds to component B.

Systems	CS^A (mm/s)	B_{hf}^A (T)	CS^B (mm/s)	$ B_{\text{hf}}^B $ (T)
V(40 Å)/Eu(200 Å)	-7.8(1)	-25.1(2)	-8.1(4)	6.8(1.1)
V(40 Å)/Eu(100 Å)	-7.9(1)	-25.5(2)	-7.4(4)	7.5(1.1)
V(40 Å)/Eu(70 Å)	-7.6(2)	-24.5(2)	-7.8(3)	8.8(1.1)
V(40 Å)/Eu(30 Å)	-7.8(1)	-24.6(3)	-7.8(3)	7.8(4)
Cr(40 Å)/Eu(30 Å)	-7.8(1)	-22.8(1.2)	-7.8(8)	7.5(3)
Fe(40 Å)/Eu(200 Å)	-7.7(8)	-23.6(1.3)	-7.3(2)	7.3(1.0)
Fe(40 Å)/Eu(100 Å)	-7.6(7)	-24.4(2)	-7.8(4)	6.8(7)
Fe(40 Å)/Eu(70 Å)	-7.7(3)	-23.7(6)	-7.8(6)	6.0(5)
Fe(40 Å)/Eu(30 Å)	-7.4(7)	-23.6(2.0)	-7.7(9)	6.2(4)
Co(40 Å)/Eu(30 Å)	-7.7(4)	-23.7(7)	-7.5(1)	4.7(5)
Ni(40 Å)/Eu(30 Å)			-8.1(1)	5.4(1)
Cu(40 Å)/Eu(30 Å)			-8.6(4)	8.9(3)
Nb(40 Å)/Eu(30 Å)			-8.3(1)	13.4(4)

observed in the spectrum which has poor statistics. The hyperfine parameters of all multilayers are given in Table I (see Figs. 5 and 6).

The ^{151}Eu CS and magnetic hyperfine field of the component B (B_{hf}^B), plotted as a function of the TM electronic configuration, for different types of TM are displayed in Fig. 7. This figure shows that until Co/Eu multilayer, B_{hf}^B smoothly decreases and CS remains constant. The CS, in

principle, is not sensitive to composition in Eu based alloys.^{7,8} On the other hand, for the Ni/Eu and Cu/Eu multilayers, the B_{hf}^B is slightly increasing and CS decreasing probably due to structural change from bcc (V, Cr, Fe) to fcc (Ni, Cu) or some solid solution formation in the Ni/Eu and Cu/Eu multilayers. The Nb/Eu multilayer has a larger B_{hf}^B and the same CS as the other Eu/TM multilayers.

The behavior of the relative area in % of the component B in the TM(40 Å)/Eu(30 Å) multilayers is also shown in Fig. 8. The relative area of component B has the maximum value for Fe/Eu multilayers indicating that in this case the Eu lay-

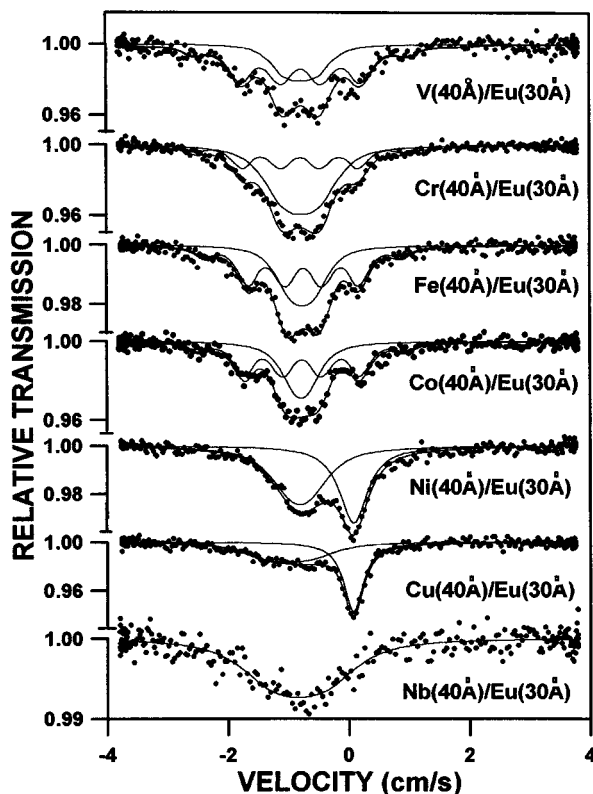


FIG. 6. ^{151}Eu Mössbauer spectra at 4.2 K for TM(40 Å)/Eu(30 Å) (TM=V, Cr, Fe, Ni, Co, Cu, and Nb) multilayers (The full lines are obtained by least square method.)

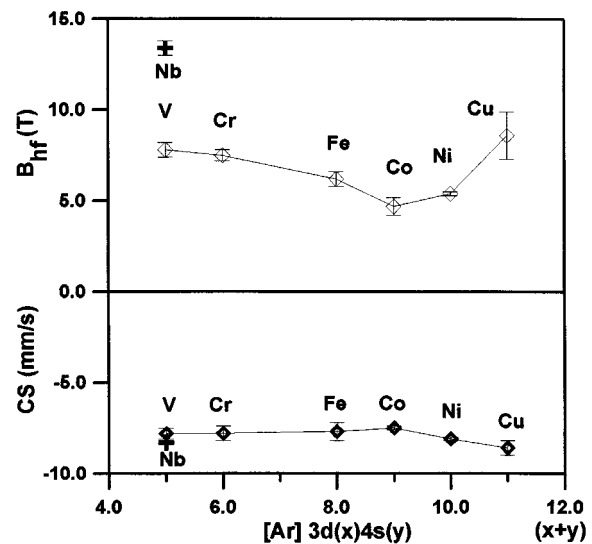


FIG. 7. B_{hf} and CS of component B against electronic configuration of the TM for Eu(30 Å)/TM(40 Å) multilayers (the dashed line is only a guide for the eyes). The “x and y” are the number of d and s electrons, respectively, while [Ar] is the configuration of argon noble gas.

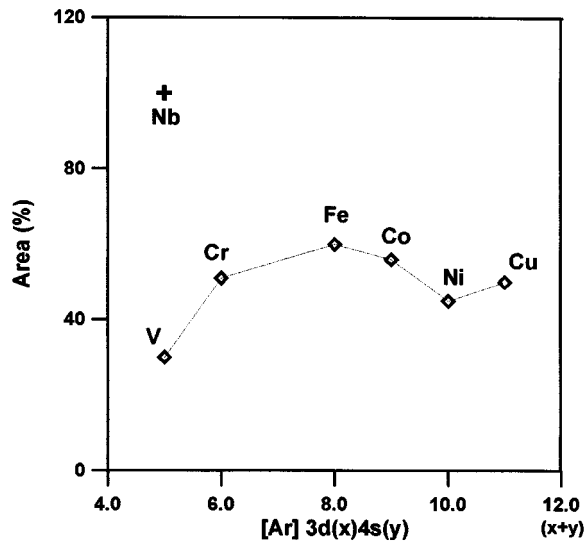


FIG. 8. Relative area of component B as a function of electronic configuration of the TM for Eu(30 Å)/Eu(40 Å) multilayers (the dashed line is only a guide for the eyes). The “ x and y ” are the number of d and s electrons, respectively, while $[Ar]$ is the configuration of argon noble gas.

ers lose the bulk magnetic properties easier than in the other systems.

V. DISCUSSION

The magnetic hyperfine field (B_{hf}) of Eu metal is commonly divided into three main contributions:⁹

$$B_{\text{hf}} = B_{\text{cp}} + B_{\text{cep}} + B_{\text{thf}}. \quad (1)$$

The first term gives the largest contribution to B_{hf} and is the core polarization field, $B_{\text{cp}} = -34.0$ T. The second term is due to the conduction electron polarization by the atom's own moment, $B_{\text{cep}} = +19.0$ T, and the last, B_{thf} is related to the transferred hyperfine fields resulting from all neighboring magnetic moments, $B_{\text{thf}} = -11.0$ T. The first term is assumed to be constant and independent of the composition in Eu alloys.⁹ In intermetallic compounds such as EuPd₂, EuPt₂, EuCu₂, etc., the last two contributions are responsible for a drastic reduction at value of B_{hf} at the Eu site.^{8,10} However, even in bulk intermetallic compounds or alloys, it is difficult to get separated information about each contribution to B_{hf} .

Since it is not clear which of the two terms, B_{cep} or B_{thf} , is responsible for the observed strong reduction of B_{hf} in the interface region, we consider the following extreme possibilities.

(1) *The reduction of B_{hf} is due to the change in B_{cep} .* In this case we have to assume that the interface region is some kind of a solid solution between TM and Eu atoms. Charge transfer between TM and Eu will change the density of states

at the Fermi level as well as B_{cep} . The systematic change of B_{hf} with the number of $3d$ electrons, see Fig. 7, seems to support this model. The conduction electron polarization, in principle, can also be changed at the interface of multilayers by strain, intrinsic interface effect, and structural change. The conventional x-ray-diffraction patterns, however, have shown that a possible structural change can occur only in Ni/Eu and Cu/Eu multilayers, but for the other TM/Eu multilayers there is no evidence of structural change or strain effect. Moreover, the pressure effect for a 10% reduction in volume does not drastically reduce B_{hf} .¹¹

(2) *The reduction of B_{hf} is due to changes in B_{thf} caused by the adjacent TM layer [via Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction].* In this case, B_{thf} would be a continuous changing function having its largest deviation from B_{thf} (Eu metal) at the interface and approaching B_{thf} (Eu metal) far away from the interface region. This model is supported by the experimental fact that the center shift in the interface region is almost independent of TM. A continuous distribution of B_{hf} (see Sec. IV) rather than separation of two components (A and B) would be suitable as a consequence of this model.

It is not possible to choose between these models because any mixture of these two extreme possibilities may occur, i.e., the reduction of B_{hf} in the interface region is due to a change of both B_{cep} and B_{thf} .

Finally we mention that the reduction of the $B_{\text{hf}}B$, in principle, could be explained by a dynamic mechanism due to the small grain size of Eu particles. In this model the Eu magnetic moments at the interface may be fluctuating even at 4.2 K. This assumption may be reasonable for [V, Cu, Nb]/Eu systems which may not have exchange energy at the interface to align the Eu moments. In the Fe/Eu case the exchange energy from the interface Fe moment would be big enough to align the Eu moments at the interface. Therefore, it seems to be difficult to explain the reduction of $B_{\text{hf}}B$ for both TM metals, magnetic and nonmagnetic, by a dynamic effect.

In conclusion our experiments show a strong reduction of the magnetic hf field at the ¹⁵¹Eu nucleus at the interface region of TM/Eu multilayers. It is not yet clear if this reduction is due to a mixture of TM and Eu atoms at the interface region or if it is caused by the adjacent TM layer via RKKY interaction.

ACKNOWLEDGMENTS

The authors thank Professor H. Micklitz for illuminating discussions and careful reading of the manuscript. Discussions with Professor A. Gomes, Dr. M. Elmassalani, and Dr. Abd-Elmeguid and help with the Eu-distribution program by Dr. R. Brand are also acknowledged. This work was supported by RHAE-NM program of MCT under the project 500938/91-1.

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