that at $\theta=0°$ the hyperfine splitting increases from series to series with increasing field strength, whereas at $\theta=90°$ it decreases.[2]

From the spectrum for $\theta=0°$ in the parallel case a simple determination of g can be made. The method entails a comparison of the position of the DPPH marker with the line $M=\frac{1}{2}\leftrightarrow M=-\frac{1}{2}$, $m=-\frac{1}{2}\leftrightarrow m=\frac{1}{2}$, which occurs ar $H=H_0-(17/2)A^2H_3^{-1}$.

If H_x denotes the position of the marker and g_x its g value then a measurement of $H-H_x$ allows us to calculate g from the equation

$$(H_0-H_x)/H_0=(g_x-g)/g_x.$$

This procedure gives the same g value as in Sec. III B.

The half-field spectrum ($\Delta M=2$) at $\theta=90°$ has also been investigated and the results are consistent with (10).

IV. DISCUSSION

The ESR spectrum of dilute manganese perchlorate is similar to that of dilute manganese fluosilicate.[2] An essential difference occurs in the relative signs of the parameters D, A, B, and a; whereas Bleaney and Ingram find D, A, B negative, and a positive in the fluosilicate, we find only relative signs; either D and a positive, A and B negative, or D and a negative and A and B positive. The magnitudes of the cubic-field parameter a, the hyperfine constants A and B, and the magnetogyric ratio g are virtually the same in both salts; the magnitude of D, however, appears somewhat smaller in the perchlorate.

A study of the parallel-field case spectra is useful as a check on the values of the parameters, especially g, and as discussed above gives a determination of the sign of D relative to A and B that is independent of second-order effects in the spectra. In general, the study of forbidden transitions can be expected to give information as to the relative importance of the various interactions in the Hamiltonian of the system. The parallel-field case is expecially well adapted to these studies because of the simplicity of the expression for the transition probabilities.

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Mössbauer Effect in Europium Alloys

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The Mössbauer effect of the 21.7-keV γ line of Eu^{151} has been employed to study the isomer shifts and the magnetic fields in Eu–Yb and Eu–Ba alloys. From these measurements the conduction-electron contribution to the hyperfine field in Eu metal due to the ion's own $4f$ electrons and due to the neighboring ions has been deduced. In addition, an explanation for the apparent lack of conduction-electron contribution to the hyperfine field in metallic Gd is offered.

1. INTRODUCTION

In magnetically ordered metals the exchange interactions between the ions take place via the conduction-electrons (CE).[1] These CE have in all cases at least some s character and thus penetrate into the atom. They have a finite density at the nucleus and their polarization gives rise to a hyperfine interaction with the nuclear moment via the Fermi-contact interaction. It is thus apparent that nuclear resonance methods are very suited for the study of the properties of the CE. NMR experiments measure the hyperfine field at the nucleus in the ordered state and from the Knight shift, the magnitude of the interaction between the electronic spins and the CE can be deduced. Mössbauer-effect studies are equally suited for the investigation of CE properties, since they measure simultaneously the charge (proportional to the isomer shift) and the spin density (proportional to the hyperfine field) at the nucleus.

Considerable information about transition metal and alloy exchange interactions[1] has been obtained by these studies. The experiments of Wertheim *et al.*,[2] Stearns and Wilson,[3] and Stearns[4] showed that an iron ion exhibits different fields when some of its neighbors are replaced by other ions. The interpretation of the experimental results is still uncertain. Whereas Wertheim *et al.*[1] consider the direct exchange between the ions to be the most important feature, Stearns[3,4] attributed these effects to the conduction electrons. By a careful analysis of the line shape of

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[1] For a survey in this field, see R. E. Watson, *Conduction Electron Charge and Spin Density Effects Due to Impurities and Local Moments in Metals in Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

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her spectra, she derived the conduction-electron spin density oscillations in iron metal.

For rare-earth (RE) bearing metals, the most detailed knowledge has been obtained from resonance experiments on RE–Al and on RE–Pd alloys.[5] The Knight shift and the g shift measurements were interpreted by assuming a uniform conduction-electron polarization. On this basis, a *negative* exchange interaction between $4f$ and conduction electrons was deduced and interpreted as being due to interband mixing.[6] On the other hand, the calculations of Freeman and Watson[7] and the hyperfine fields in Eu and Gd intermetallic compounds,[8] which are less negative than the corresponding fields in a diamagnetic ionic impurity, suggest a *positive* CE polarization at the site of the nucleus of the magnetic ion. These two findings are not necessarily contradictory. The CE polarization is known to exhibit an oscillatory behavior as a function of the distance from the nucleus of the magnetic ion.[9] Thus, even though the CE polarization created at the nucleus of an ion by its own magnetic electrons is positive, a neighboring ion (e.g., Al in the $REAl_2$ compounds), lying in a region of negative spin density, will exhibit a Knight shift which is interpreted as being due to a negative CE polarization.

The present experiment was undertaken in order to investigate this question for Eu alloys. Eu is well suited for such an investigation because the 21.7-keV γ-ray transition in Eu^{151} is very favorable for Mössbauer-effect studies. Eu atoms, when divalent, are in an $^8S_{7/2}$ ground state. The orbital contributions of the $4f$ electrons to the observed hyperfine fields are therefore negligible. To separate the contributions to the hyperfine field at the Eu nucleus in an alloy due to the ion's $4f$ electrons from those which come from the neighboring ions, one has to increase the distance between Eu ions till the effects of the neighbors vanish. However, in so doing, it is necessary that the band structure of the CE be affected as little as possible. This is most easily done by diluting Eu metal with Ba and Yb ions, which have the same electronic structure as Eu except for the $4f$ shell. Divalent Ba and Yb are essentially diamagnetic.

The results of our Mössbauer-effect studies on Eu–Ba alloys and Eu–Yb alloys are reported below. From these studies, it can be concluded that while the CE polarization at the nucleus due to the ion's own $4f$ electrons is positive, the contributions due to the neighbors are negative.

2. EXPERIMENTAL RESULTS

The Eu–Ba and Eu–Yb alloys were prepared by induction-melting the stoichiometric amounts of the two metals in ceramic crucibles in an argon atmosphere. The actual composition and the homogeneity were checked by X-ray fluorescence and by microprobe analysis. No difficulty was encountered in the preparation of the Eu–Yb alloys. In the case of the Eu–Ba alloys, with increasing Ba content, an increasing contamination of the samples with EuO could not be avoided. Presumably this was due to a reduction of the ceramic by the Ba. It was therefore decided not to use the results obtained for the alloys containing more than 50% Ba because in these the EuO contamination exceeded 10%.

The absorbers with approximately 30 mg of Eu^{151} per cm^2 were prepared by rolling lumps of the alloys under oil. In this way the EuO contamination (the major impurity) could always be kept below a few percent. It is very difficult to estimate the actual impurity concentration. Although the most accurate determinations of the impurity line areas are made at $T > 77$°K because of the absence of magnetic splitting, the widely different Debye-Waller factors

$$[\Theta_D(\text{Eu metal}) \approx 100°\text{K},\ \Theta_D(\text{EuO}) \approx 250°\text{K}]$$

make it difficult to accurately relate the areas under the absorption lines to the actual composition of the samples.

The spectra were obtained in a standard transmission geometry with a setup similar to that described previously by Cohen *et al.*[10] The samples were immersed directly in liquid helium. The spectra of the two lowest Yb concentrations were obtained at 1.7°K. For the determination of the Curie temperatures the samples were fixed to the cold finger of a Dewar which was filled either with liquid helium or liquid hydrogen. The Curie temperatures were determined from the onset of magnetic broadening in the spectra.

Figure 1 gives a number of Mössbauer absorption spectra of EuYb alloys taken approximately at a temperature where magnetic saturation is reached (4.2°K, except for the two highest Yb concentration). The solid lines are least-square fits of theoretical curves to the experimental points. The fits were performed by assuming one magnetic field at the Eu nucleus. Table I gives the results for the Eu–Yb system. The

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TABLE I. Experimental results on the Eu–Yb system.[a]

Composition	T (°K)	$-H_{\rm eff}(T)$ (kOe)	$-H_{\rm eff}$ ($T=0$°K)	Γ (mm/sec)	T_c (°K)	ISM[b] (mm/sec)
$Eu_{1.00}Yb_{0.00}$	4.2	264_5	265_5	1.3_1	90_2	-8.3_3
$Eu_{0.92}Yb_{0.08}$	4.2	257_5	258_5	1.5_1	83_3	-8.3_3
$Eu_{0.76}Yb_{0.24}$	4.2	244_5	246_5	1.7_1	69_3	-8.2_3
$Eu_{0.57}Yb_{0.42}$	4.2	238_5	240_5	1.6_1	48_3	-8.3_3
$Eu_{0.46}Yb_{0.56}$	4.2	210_8	213_9	1.6_1	35_3	-8.1_3
$Eu_{0.37}Yb_{0.63}$	4.2	188_8	195_9	1.7_1	18_3	-8.1_3
$Eu_{0.19}Yb_{0.81}$	1.7	171_8	173_9	1.5_1	10_2	-8.1_3
$Eu_{0.08}Yb_{0.92}$	1.7	140_9	160_9	1.9_1	5_2	-8.6_3

[a] Subscript gives error in the last significant figure. [b] Isomer shift.

magnetic fields extrapolated to 0°K were obtained by using the experimentally determined Curie temperatures and a Brillouin function for $S=\frac{7}{2}$. This procedure is certainly accurate within a few kOe, the accuracy with which the magnetic fields could be obtained experimentally. The linewidths that were obtained from the fits varied only slightly but not systematically through the alloy series. Since the samples were not perfect but always contained slight amounts of impurities we will draw no conclusions from the difference in linewidth of the various samples. It should also be mentioned that due to the chemical properties of Eu, it was not possible to anneal the foils after rolling. Consequently, strains and imperfections could also contribute to the linewidth.

Figure 2 shows some spectra obtained for alloys in the Eu–Ba system. They are very similar to the Eu–Yb alloys, except for slight asymmetries due to

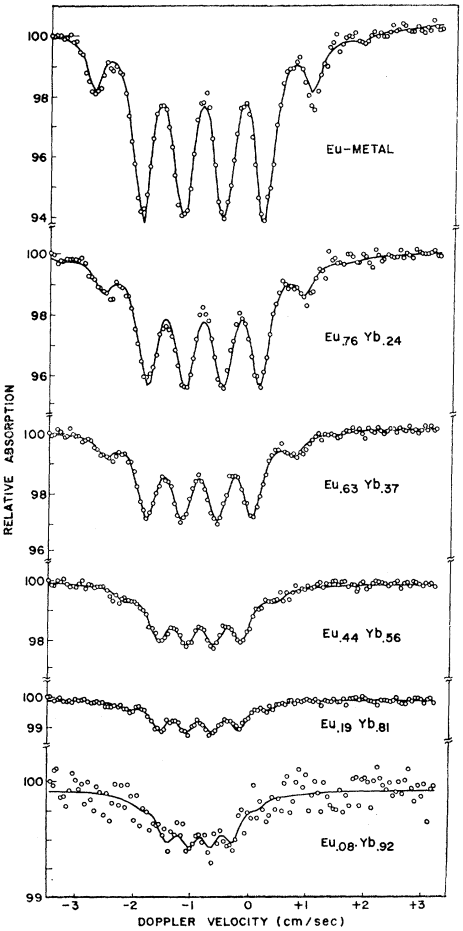

FIG. 1. Mössbauer absorption spectra for the 21.7-keV γ line of ^{151}Eu in the $Eu_{1-x}Yb_x$ alloy system.

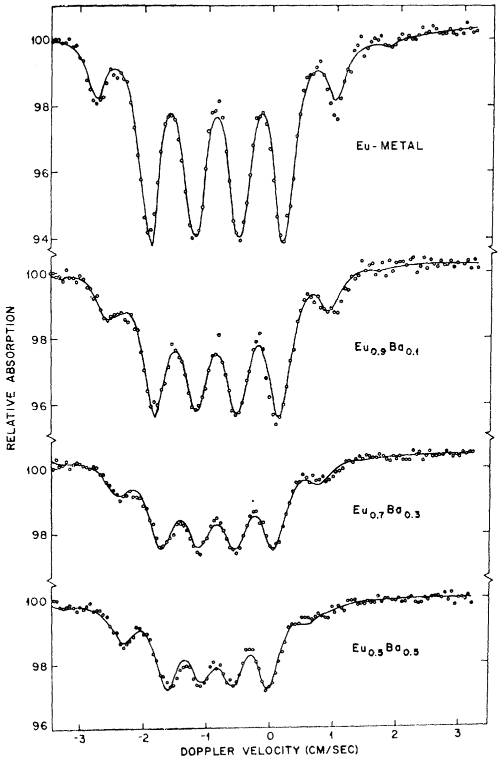

FIG. 2. Mössbauer absorption spectra for the 21.7-keV γ line of ^{151}Eu in the $Eu_{1-x}Ba_x$ alloy system.

TABLE II. Experimental results on the Eu–Ba system.[a]

Composition	T (°K)	$-H_{\text{eff}}$ (T°K) (kOe)	$-H_{\text{eff}}$ (T=0°K)	Γ (mm/sec)	T_c (°K)	ISM (mm/sec)
$\text{Eu}_{1.0}\text{Ba}_{0.0}$	4.2	264_5	265_5	1.3_1	90	-8.3_3
$\text{Eu}_{0.9}\text{Ba}_{0.1}$	4.2	248_6	249_6	1.6	80	-8.3_3
$\text{Eu}_{0.8}\text{Ba}_{0.2}$	4.2	242_6	244_6	1.9_1	70	-8.3_3
$\text{Eu}_{0.7}\text{Ba}_{0.3}$	4.2	228_6	230_6	1.9	60	-8.3_3
$\text{Eu}_{0.6}\text{Ba}_{0.4}$	4.2	213_6	216_6	1.9_1	50	-8.3_3
$\text{Eu}_{0.5}\text{Ba}_{0.5}$	4.2	203_6	206_6	1.8_1	40	-8.3_3

[a] Subscript gives error in the last significant figure.

EuO contamination. In this case the fits (solid lines) were performed by allowing for these impurities; it can be seen that then the calculated curves agree very well with the measured ones. Table II gives the results on the Eu–Ba system. In this case we give the composition to only one significant figure because of the previously mentioned difficulty of getting a very accurate value for the content of EuO. The Curie temperatures in this case are extrapolated values from those obtained for the Eu–Yb system.

Figures 3 and 4 show graphically the relevant results obtained from (Tables I and II) the experimental spectra for the two alloy systems. The slight discontinuity in the concentration dependence of the hyperfine fields and the Curie temperatures for the Eu–Yb system at around 50%, is due to a change in crystal structure from the bcc Eu structure to the fcc Yb structure which takes place in this region.

3. DISCUSSION

The most obvious fact deduced from the spectra in Figs. 1 and 2 is that, at all concentrations, one is dealing with spectra produced by essentially a single magnetic field. From this, one can conclude that the exchange interactions in these alloy systems are of long range. For the case of only short-range interactions, one would expect to see in the region of 50%

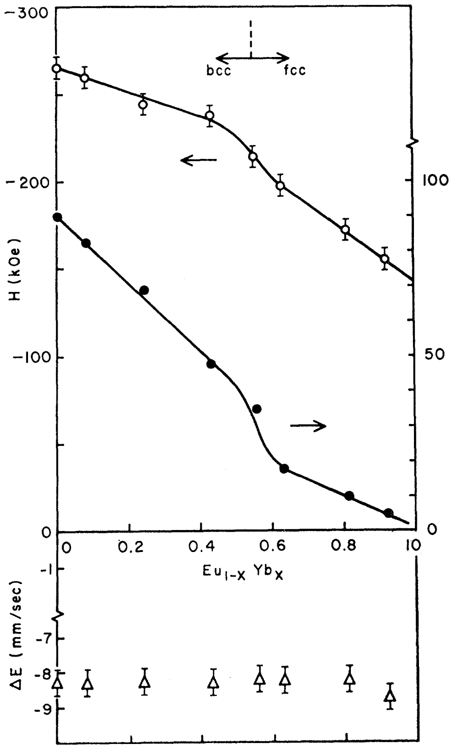

FIG. 3. Hyperfine fields, isomer shifts, and Curie temperatures of the $\text{Eu}_{1-x}\text{Yb}_x$ alloy system.

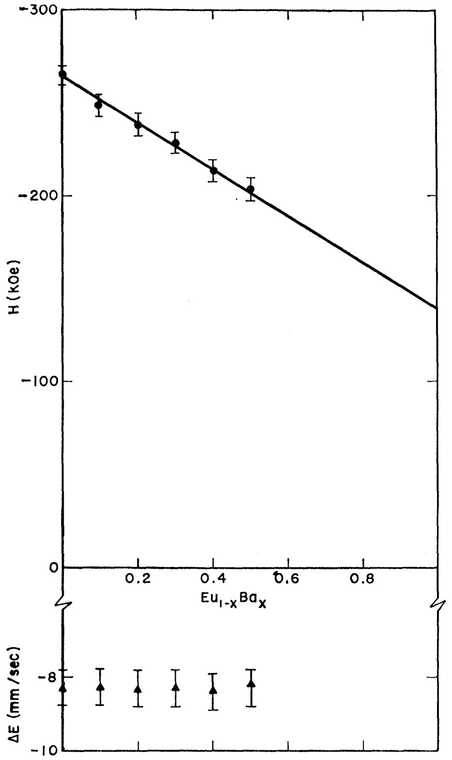

FIG. 4. Hyperfine fields and isomer shifts for the $\text{Eu}_{1-x}\text{Ba}_x$ alloy system.

concentration a distribution of hyperfine fields. Our result is in agreement with the neutron diffraction measurements of Shirane and Pickart,[11] who found in a series of Er–Ho alloys that the cone angle changed smoothly with concentration and that there were no distributions of cone angles. This result was interpreted as evidence of a long-range exchange interaction in rare-earth metals and alloys.

The hyperfine fields in the alloy systems studied in this work *decrease* (in absolute value) with *increasing* dilution. The field value obtained after extrapolating to 100% Yb or Ba content is about −150 kOe. The hyperfine field of Eu^{2+} in the diamagnetic *insulating* host CaF_2 is −340 kOe.[12] The negative sign of the fields in Eu metal and of Eu^{2+} in different environments has been determined by Passel *et al.*[13] by a neutron diffraction experiment.

There still seems to be some controversy as to the origin of this field. Baker and Williams[12] have discussed the factors contributing to the hyperfine field of Eu^{2+} in CaF_2 and have concluded that about −260 kOe are of s character and −80 kOe are of f character. The latter contribution comes about by deviations from the Russel-Saunders coupling, which mixes a small amount of $^6P_{7/2}$ state into the ground state. The position of the excited $^6P_{7/2}$ state does not vary for different compounds. Therefore its admixture to the ground state and hence the f contribution to the hyperfine field does not vary. This leads one to the conclusion that the value of −340 kOe can be taken as a constant for Eu^{2+} in different ionic environments.

On the other hand, Winkler,[14] from his analysis of all available hyperfine-structure measurements in Eu, concludes that the core-polarization value for Eu^{2+} is −350 kOe, thus leading to a negligible f contribution to this field. It should also be mentioned in this context that Wybourne,[15] in a very detailed investigation, was unable to find a satisfactory explanation for the crystal-field splitting in Gd salts. He considered especially the admixtures of the $^6P_{7/2}$ level, which Baker and Williams[12] consider responsible for the f contribution to the hyperfine fields, and finds that they cannot account for the observed zero-field splitting.

Thus, we are left with the conclusion that the origin of the field of −340 kOe is not yet clear, though its main contribution most certainly comes from the core polarization, and its magnitude is little affected by the chemical environment. Hence, for our further discussion, we will call this field the core-polarization contribution and assign it a value of $-(340\pm20)$ kOe.

For our alloy systems the isomer shift, and hence the charge density at the nucleus, stays essentially constant. The decrease in hyperfine field therefore reflects an increase in spin-polarization, because there is no additional orbital contribution to the hyperfine field created by the dilution. The magnetic field at the nucleus of an Eu^{2+} ion in a metallic environment is the sum of the following terms:

(1) Core polarization $[-(340\pm20)$ kOe$]$. It can be assumed that this contribution is roughly constant for all the alloys investigated.

(2) CE polarization. (a) Polarization by the $4f$ electrons of the ion itself. Since we assume that the diluents Ba metal and Yb metal have the same band structure as Eu metal, this contribution also has the same value for all the alloys investigated. (b) Polarization of the CE by the $4f$ electrons of all the neighbors. Since in going from Eu metal to $Eu_{0.08}Yb_{0.92}$, for example, the average distance between two Eu ions is more than doubled, we assume that this contribution to the hyperfine field is reduced as one goes from Eu metal to $Eu_{0.08}Yb_{0.92}$.

(3) Overlap and covalency contributions from the neighbors. It can be assumed that these contributions are only of the order of 1 kOe or smaller since it has been found to date that transferred hyperfine fields are very small in rare-earth compounds.[16] It can also be assumed that this contribution gets smaller with increasing dilution.

Contributions (2) and (3) consist of a direct term and an indirect one via the polarization of the closed s shells of the ion. We assume now that the value of −150 kOe, obtained by extrapolation to zero Eu content, is the sum of contributions (1) and (2a), since they are not affected by dilution. This gives a value of +190 kOe for the CE polarization at the nucleus of an ion by its own $4f$ electrons. The field of −115 kOe, which is the difference between the observed field of 265 kOe in Eu metal and the two contributions just considered, is then ascribed to neighbor effects [contributions (2b) and (3)]. Because of the small contribution of covalency and overlap, this −115 kOe field is almost entirely due to CE polarization. Table III summarizes the various contributions to the hyperfine field in Eu metal.

The value of the field at the nucleus for the neutral Eu atom ($4f^7\,6s^2$) is −70 kOe,[17] as compared to −150 kOe for dilute Eu^{2+} in a metallic environment with the $6s^2$ electrons in the conduction band. So, the polarization of the atomic $6s^2$ by the $4f^7$ electrons is about 270 kOe and only roughly 35% higher than

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TABLE III. Analysis of the hyperfine fields in Eu metal and Gd metal.

	H_{eff} (kOe) Eu	H_{eff} (kOe) Gd
Core polarization	$-(340\pm20)$[a]	$-(340\pm20)$[b]
Conduction-electron polarization by own $4f$ electrons	$+(190\pm20)$[c]	$+(240\pm50)$[c]
Neighbor effects: conduction-electron polarization+overlap+covalency	$-(115\pm20)$[c]	$-(200\pm60)$[d]
Metal	$-(265\pm5)$[e]	$-(350\pm35)$[f]

[a] References 12 and 13.
[b] References 18 and 13.
[c] Present work, see text.
[d] Reference 20.
[e] Reference 13 and present work.
[f] Reference 18.

that of the $6s^2$ electrons in the conduction band. This is a good indication that even in a metallic environment a rare-earth ion behaves very much like a free ion. That this is true in insulators has been known for a long time.

The above results are in agreement with the *negative* exchange integrals derived at the site of the diamagnetic diluents.[5] Comparing this result with the susceptibility-enhanced spin density calculations of Watson and Freeman,[7] we find qualitative agreement for a value of k_F of about 0.7 a.u.

Interpretation of the hfs Field in Gd Metal

In view of these findings for Eu metal we want to propose the following interpretation for the hyperfine field in Gd metal, which is known to be $-(350\pm35)$ kOe.[18] Comparing this value with the fields of Gd^{3+} obtained in various diamagnetic hosts (all are about the same value), Shore *et al.*[18] concluded there was a very small (of the order of a few percent) contribution of the CE to the hyperfine field in Gd metal.

For the core polarization in Gd^{3+} we adopt the value of -340 kOe obtained by Hempstead and Bowers[19] in $CaWO_4$. Values obtained in different environments agree within experimental error with this value, but are generally less accurate. We shall attribute an error of ±20 kOe to that figure, to account for possible effects of covalency. As in the case of Eu^{2+}, we are not sure whether this field is entirely due to core polarization, or contains slight f-electron contributions due to deviations from Russel-Saunders coupling. Since it does not change substantially with environment we shall call it the core-polarization value.

We estimate the value of the hyperfine field, due to the CE polarization at the site of the Gd ion by its own $4f$ electrons, to be $+(240\pm50)$ kOe. This is obtained by utilizing our estimated value of $+190$ kOe for this contribution in Eu metal (2 conduction electrons as compared to 3 for Gd), and allowing for a reduction due to the d character of the CE in Gd metal. (The limits of error were set to include the two limiting cases: no s character at all for the additional electron, or all s character.) Now, the contribution to the hyperfine field by neighboring atoms (-200 ± 60 kOe) has been obtained by Cohen *et al.*[20] by measuring the field at the site of diamagnetic Lu (band structure similar to Gd metal) in Gd metal. Thus, the two contributions approximately cancel, making the hyperfine field in Gd metal approximately equal to the core-polarization value. Table II summarizes the various contributions to the hyperfine fields in Gd metal.

We want to draw the attention to two additional interesting features. Within our accuracy the isomer shifts, i.e., the charge densities, are constant and the same in the Eu–Yb system and the Eu–Ba system. This is somewhat surprising in view of d admixtures for RE conduction bands, which should be smaller for Ba metal. Either there is an accidental cancellation of some terms or, at least for the divalent RE, the d character of the CE band is not very pronounced.

Secondly, the hyperfine fields are the same for the bcc EuYb alloys and EuBa alloys. This shows that the polarization of the closed $4f$ shell of the Yb ions by the CE or by direct overlap, contributes only little to the magnetic properties of the system.

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