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Hyperfine fields at nonmagnetic atoms in metallic ferromagnets

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The various models used to describe the hyperfine field at nonmagnetic impurities in metallic ferromagnets are discussed. These models fall into two main categories. In one the impurity is considered to introduce a strongly perturbing charge disturbance and solute-host effects are nonseparable. These models use scattering-theory concepts and formalism and the host and impurities are represented by parameters which are difficult to relate to, and often in conflict with other known information about these systems. In the other approach the perturbation of the *s*-conduction-electron polarization caused by the solute is considered to be small enough so that the hyperfine field at the impurity can be separated into a host *s*-conduction-electron polarization contribution and a contribution associated with the impurity atom. This model is formulated in terms of atomic and band properties and thus can give information about the impurity and host wave functions. This separable volume misfit model is modified from earlier presentations to take into account the changes in the *d*-conduction-electron polarization in the vicinity of impurity atoms with *d* valence electrons. The impurity contribution, also known as the transferred hyperfine field or volume overlap contribution, has been calculated for the 4*sp* and 5*sp* solute atoms in Fe. The main differences from previous calculations of this type are that in order to better represent the solid state of the host we have used a more diffuse 3*d* orbital for the Fe atoms which closely resembles the Fe band orbital. We have also included contributions from the 2nn (2nd nearest neighbor) and 3nn shells. With these improvements we get excellent agreement between the experimental solute-atom contribution obtained from the volume misfit model and the calculated overlap hyperfine fields.

I. INTRODUCTION

Many models[1–7] have been proposed to explain the hyperfine-field (hff) values at nonmagnetic atoms in a metallic magnetic environment. The nonmagnetic atoms can occur as either impurity atoms in a magnetic host or as a nonmagnetic constitute in a magnetic compound, such as in Heusler alloys. Many of these proposed models have considered only part of the contributions to the hff and, therefore, are destined to give incorrect hff values upon wider application. Another fallacy, not of direct concern in this paper but often encountered in the application of various models,[2] is the assumption that the interaction which gives the dominant contributions to the hff (i.e., the interaction with *s*-like electrons when the orbital momentum is quenched) also determines the magnetic transition temperatures. We have seen[5,8] that in Fe the d_i-d_l Coulomb exchange interaction between the itinerant, d_i, and localized, d_l, *d*-like electrons causes the magnetic alignment and thus determines the magnitude of the transition temperature, *not* the *s*-*d* interaction. This is also expected to be the usual situation in other metallic *nd* magnetic materials.

There have been essentially seven contributions to the hff discussed in the literature. Many of these are interrelated and we shall try to clearly indicate these relations. Figure 1 gives a schematic representation of these contributions and a classification of the various models. The models that have been proposed differ in their basic assumptions.

Models indicated by the line to the left are based on scattering-theory concepts and formalism and assume that the hff comes entirely from conduction-electron-polarization (CEP) effects. They assume that all the valence electrons of *sp* impurity atoms become conduction electrons. This leads to a strong perturbation in the *s*-CEP which depends on ΔZ, the difference in the number of valence electrons of the impurity atoms and the host atoms. The origin of models of this type is founded in the behavior of the residual resistivities of *sp* impurities in Cu, Ag, and Au. These were experimentally[8] seen to be proportional to $(\Delta Z)^2$. Thus the scattering amplitudes of the impurity atoms in nonmagnetic systems was found to be proportional to ΔZ. However the situation in magnetic hosts is much more complex. Here the residual resistivities[9] are spin dependent due to the added exchange scattering from the moment perturbation caused by the impurity.[10] So the scattering amplitude is no longer simply proportional to ΔZ. A shortcoming of these hyperfine-field models is that the scattering-theory formalism is developed in terms of parameters which are hard to relate to other measured properties. Thus it is difficult to obtain any in-

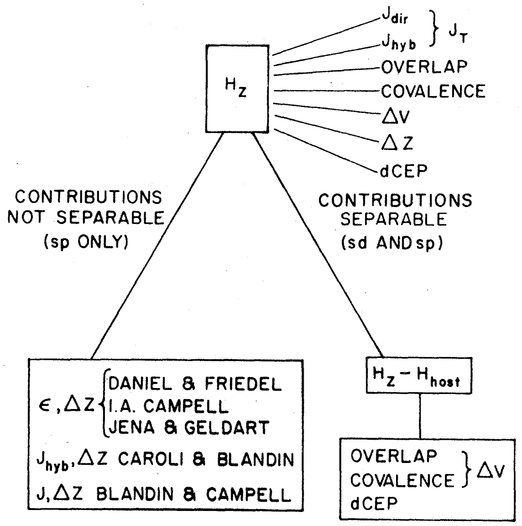

FIG. 1. Diagram representing the various hff contributions and their relationships in different proposed models.

formation from these analyses. The underlying assumptions and interpretation of these models are discussed in Sec. III.

The models indicated by the line to the right assume that the hff at a nonmagnetic impurity can be separated into two contributions: One is the *s*-CEP contribution inherently present in the magnetic host. The other is a contribution which is associated directly with the impurity atom and arises from the volume overlap or transferred hff between the impurity and its nearby host atoms (volume misfit model). Thus this model differs greatly from the nonseparable models in its basic assumptions about how the valence electrons behave in solids. It assumes that substitional impurity atoms in host transition metals tend to look much like a host atom. Thus each impurity contributes only about one *sp*-like electron to the conduction band of the host. The other *sp* electrons stay mainly in the vicinity close to the impurity atom shielding its excess charge and do not perturb the host *s*-CEP appreciably.

Evidence that the charge perturbation does not affect the host *s*-CEP is that the hff changes at Fe atoms which are near neighbors to an impurity atom are essentially independent of the number of valence electrons of the impurity.[11-13] This indicates that the *s*-CEP in the vicinity of the impurity is quite independent of the valence of the impurity. Further evidence is that *s*-CEP of the Heusler alloys $X_2\text{Mn}Y$ is essentially independent of the number of valence electrons of the Y element.[6,14] This indicates that the Y atoms contribute about the same number (~ one) of *sp*-like electrons to the conduction band, independent of their number of valence electrons. Thus, although there may exist charge perturbations and oscillations in the charge density surrounding an impurity atom, their affect on the *s*-CEP is considered to be secondary. The great advantage of the separable model is that the *s*-CEP contribution due to the host can be subtracted from the measured hff leaving a contribution which is due to the interaction of the electronic structures of the host and impurity atom. This then gives us the possibility of obtaining information about the wave functions of the host and impurity atoms from hff measurements.

In the case of a small impurity atom having negligible overlap with the host atoms (and no charge perturbation since the size and number of valence electrons are directly connected), e.g., Cu, Ag, and Au in Fe, both models should give essentially the same result. We will thus discuss the host contributions first and then the impurity-atom contributions.

A. Host contributions: J_{dir} and J_{hyb}

The contributions associated with the host are the Coulomb exchange interactions, J_{dir} and J_{hyb}.

1. J_{dir}

This is the *s*-CEP from direct Coulomb exchange interactions between the *s*-like conduction electrons and the localized *d* electrons, the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction.[15] This interaction is expressed in terms of an exchange integral between one-electron orbitals which is positive definite,[16] i.e., $J_{\text{dir}}(q=0) > 0$. The *s*-CEP from this term is oscillatory in real space and has a net positive polarization.

It had been observed that some local moments, especially the rare earths, produce a net negative *s*-CEP, so in these cases some other mechanism has to be dominant. Thus it was realized that there was a second contribution.

2. J_{hyb}

This contribution is from the interband mixing[17,18] or hybridization. Its origin arises from the deviation of the valence-electron wave functions from spherical symmetry due to the atoms being confined to the lattice of a solid. Thus in the condensed state rather large nonzero hybridization matrix elements occur. The spin dependence of these terms is due to the exclusion principle and in this sense the hybridization term has the same origin as the direct exchange and is often referred to as the indirect exchange interaction. It is often treated using partial-wave scattering analysis where the hybridized states are called virtual-bound levels or resonance states.[1,2,19] This interaction has received much attention in its complementary role of magnetic impurity atoms in nonmagnetic hosts. There, its character of having a net negative exchange intergral, $J_{\text{hyb}}(q=0) < 0$, gives rise to

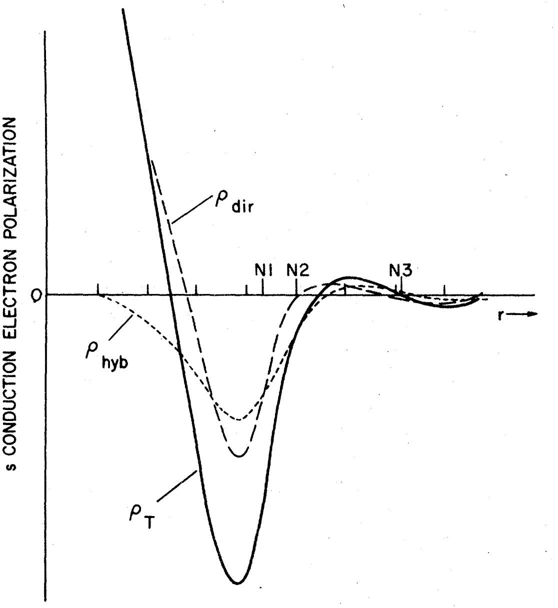

FIG. 2. Typical s-conduction-electron polarizations due to direct Coulomb exchange, ρ_{dir}, and indirect interband mixing, ρ_{hyb}, and their sum ρ_T as a function of distance. (For a conduction-electron density of about 1 electron/atom in Fe.) $N1$, $N2$, and $N3$ show the distances of the first-, second-, and third-near-neighbor shells.

the well-known resistance minima.

The most thorough theoretical investigations of the behavior of these s-CEP oscillations have been given in a series of papers by Watson *et al.*[20–23] In general they found oscillatory behavior as shown in Fig. 2 by ρ_{hyb}. For ρ_{hyb} conduction-electron density of about one electron per atom, as in Fe, the direct Coulomb exchange spin density, ρ_{dir}, is positive in the intra-atomic region and negative in the region of the first and second neighbors. The interband mixing spin density, ρ_{hyb}, is negative in the intra-atomic region as well as the region of first and second neighbors, as shown in Fig. 2. The total is as shown in Fig. 2. Its shape, as shown, is similar to the experimental measurements on Fe and its alloys.[5,11] There, of course, only the total, ρ_T, is measured. The experimental measurements have given two important results: (i) The first is that the *net polarization of the s-CEP is very small,*[11,24] *thus* $J_{hyb} \simeq -J_{dir}$. This behavior is also seen in the calculation by Watson *et al.*[23] for Gd which gave $J_{hyb} \simeq -0.85 J_{dir}$. It is interesting to compare this with the results of a thorough analysis by Walstedt and Walker[25] of many types of experiments on Mn in Cu which gave $J_{dir} \simeq 0.1$ to 0.2 eV and $J_{hyb} \simeq -0.4$ eV. (ii) The second result is that the s-CEP is negative[11] (i.e., aligned opposite to the local moments) in the region of the first and second neighbors where it is largest. This shows that the s-CEP is *not* responsible for aligning the localized moments and thus does not determine the magnetic transition temperature.

We can see how the direct exchange and hybridization interactions give contributions of opposite sign to the interaction energy and thus have very little effect on the alignment. The total interaction energy from the s electrons is found by summing over the lattice. Thus

$$\begin{aligned} E^s_T &= \sum_n E(\vec{r}_n) \\ &\simeq -\sum_n M_n [J_{dir} \vec{S}_n \cdot \vec{\rho}_{dir}(\vec{r}_n) \\ &\qquad + J_{hyb} \vec{S}_n \cdot \vec{\rho}_{hyb}(\vec{r}_n)] \ . \end{aligned}$$

For Fe we have seen the $J_{dir} \simeq -J_{hyb}$ and $\rho_{dir}(r_1) \simeq \rho_{hyb}(r_1)$. Since the s-CEP is appreciably greater for 1nn sites than higher neighbors, we have $E^s_T \simeq 0$.

B. Impurity-atom contribution; ΔZ, ΔV, overlap, covalence, and d-CEP

These terms depend very fundamentally on the electronic structure of the impurity atom. Thus to some extent they are all interrelated.

1. ΔZ

As indicated by the box on the lower left of Fig. 1, a number of workers[1,4,6,7] have assumed that the s-CEP is strongly dependent on the valence-electron difference, ΔZ, of the impurity atom and the host. The presence of the impurity atom is represented by a spin-independent square-well potential which is modified in various ways to introduce spin-dependence due to the presence of host magnetic atoms. The s polarization is obtained by using scattering-theory formulation and the Friedel sum rule to determine the phase shifts. As indicated by the large number of authors in the left box in Fig. 1 various approximations and interpretations are made in this model. These, and the resonance model of Ref. 2, will be discussed further in Sec. III.

2. ΔV

One of us (M.B.S.) proposed[5] a model where the host s-CEP contribution, H_h, was assumed to be independent of the impurity atom and thus separable. It was thus subtracted from measured hff, H_Z, in order to examine the contribution, H_i, due to the impurity atom. It was noted that the H_i values obtained in this way were usually positive and their variation with atomic number Z was similar to that of the atomic volumes. Thus it was suggested that this term could be approximated by the simple form

$$H_i = \text{const} A_Z (V_Z - V_0) \ , \qquad (1)$$

where A_Z is the hyperfine coupling constant for the valence s electrons and V_0 is a volume associated with the host, such that if the atomic volume, V_Z, of the impurity atom in its own environment were greater than V_0, the impurity atom would obtain an additional hff given by Eq. (1). In detail the H_i term is due to the interaction of the impurity and host electrons, including the lattice distortions introduced by the impurity atom. In the form given in Eq. (1) it is explicitly assumed that all impurity atoms contribute the same number of *sp*-like electrons (~ 1 in an Fe host) to the conduction band while the rest of the impurities valence electrons remain within the impurity unit cell shielding its nuclear charge.

3. Overlap and covalency

The volume misfit model is closely related to the transfer hff mechanism discussed by Watson and Freeman[26] and proposed by Shirley[3] as the mechanism responsible for the hff of *sp* impurities with $H_Z > 0$. Shirley, however, did not subtract out the contribution from the s-CEP of the host. In the more complete discussion of transfer hff given in Ref. 26 two effects are discussed; overlap and covalency. The overlap term is obtained by orthogonalizing the occupied orbitals of the solute and host atoms and is what Shirley estimated. The so-called covalent term occurs because the system is magnetic. It arises from the mixing of the occupied and empty orbitals of like spins of the impurity and host atoms. This mixing occurs to the degree that it lowers the energy of the system. Hafemeister[27] and Sondhi[28] have made more complete calculations of the volume overlap contribution. However they used atomic wave functions which, as expected, led to overlap contributions which were much too small. In Sec. IV we present similar calculations of the overlap or transferred hff contributions in which we have tried to better represent the environment that the host is in in the solid state by using more diffuse $3d$ orbitals which more nearly resemble the Fe band orbitals. Overlap and covalency effects give positive contributions to the hff at the impurity. In Sec. II we further discuss the volume misfit model and in Sec. III the charge perturbation models. The effects of the d-CEP for impurities having an appreciable number of d_i conduction electrons is also discussed in Sec. II.

II. HOST AND IMPURITY CONTRIBUTIONS SEPARABLE: VOLUME MISFIT MODEL

As previously discussed, in this model it is assumed that the s-CEP from the host is essentially unaffected by the impurity atom; thus the host and impurity contributions are separable and additive. Additivity should be a reasonably valid assumption since the polarization contributions per magnetic host atom are at most about 1.5% for s-CEP and 1% for impurity-host overlap. The hff measured at a nonmagnetic impurity atom of atomic number Z is thus given by

$$H_Z = H_h + H_i \ , \tag{2}$$

where H_h is the sum of the s-CEP contributions at the impurity due to the surrounding magnetic moments. It is given by $H_h = \Sigma M_n H_n$, where H_n is the s-CEP hff contribution from a host atom in the nth neighbor shell surrounding the impurity atom and M_n is the number of atoms in that shell. Under the assumption that the s-CEP is unchanged by the presence of the impurity atom, H_h can be obtained from the host hff due to the neighboring magnetic host atoms. This has been measured for an Fe host and is ~ -150 kG.[9,29] We then obtain H_h by making the reasonable assumption that the outer electrons are very atomic-like when near the nucleus. Therefore the s-like conduction electrons have the character of the host s-like valence electrons when near a host nucleus and that of the impurity s-like valence electrons when near an impurity nucleus. H_h is then given by

$$H_h = H_h^{\text{host}} A_Z / A_{\text{host}} \ , \tag{3}$$

where A_Z is the hyperfine coupling constant which is the value of the hff at a nucleus due to a valence electron of one unpaired spin. It is a direct measure of the probability of an ns electron being at the origin, $\psi_{ns}^2(0)$. A_Z values have been calculated and tabulated by several authors.[4,30] In general these calculations have been made using various atomic basis functions and the A_Z values vary slightly due to this. However the relative values of any set of A_Z values are quite independent of the basis set. In reality the A_Z values used in Eq. (3) should be those of an atom in a solid rather than a free atom. These are expected to be somewhat smaller than those of free atoms. However the difference between A_Z values for free atoms and atoms in the solid state is expected to be systematic and largely cancel out of a ratio of A_Z values. Thus the error made in using atomic A_Z values for the ratio in Eq. (3) is expected to be small.

We have neglected any non-s orbital contributions. Generally these are small and where measured,[31] e.g., for Au, a correction can be made. In any case, for elements other than the noble and alkali metals, the A_Z values are not known accurately enough at this time to warrant concern about orbital terms. The host which has been studied most is Fe. Co and Ni as well as Heusler-alloy hosts behave in a very similar manner to Fe. We will thus consider mainly a Fe host here, but a similar treatment should be applicable to the other hosts. In Table I we list the measured[32] H_Z and H_h values calculated from Eqs. (2) and (3). We see that often the H_h values are large causing the H_i values to be very different from the measured H_Z values. Thus, comparing a calculated

TABLE I. Hyperfine-field values at nonmagnetic impurities in Fe.

Z		H_z[a]	H_h^Z	H_i^Z
19	K	−73(6)	−45	−25
20	Ca	−103(4)	−60	−40
21	Sc	−100(5)	−70	−30
22	Ti	−130(15)	−80	−50
29	Cu	−220(4)	−220	0
30	Zn	−102(15)	−270	+170
31	Ga	(−)117(3)	−415	+300
32	Ge	+46(5)	−580	+625
33	As	+333	−760	+1090
34	Se	+680(50)	−970	+1650
35	Br	(+)830(120)	−1200	+2030
39	Y	−293(5)	−190	−100
40	Zr	(−)132	−205	(+)70
47	Ag	−454(2)	−400	−50
48	Cd	−347(2)	−480	+135
49	In	−295(6)	−700	+405
50	Sn	−88(3)	−920	+830
51	Sb	+227(5)	−1160	+1390
52	Te	+670(4)	−1430	+2100
53	I	+1137(2)	−1725	+2860
54	Xe	(+)1540(100)	−2050	+3590
55	Cs	+266(10)	−150	+420
56	Ba	−92(14)	−250	+160
57	La	(−)157(30)	−355	+200
72	Hf	−610(70)	−710	+100
73	Ta	−663(13)	−790	+125
74	W	−650(13)	−950	+300
79	Au	−1500(30)	−1620	+120
80	Hg	−845(8)	−1975	+1130
81	Tl	−190(70)	−2525	+2335
82	Pb	+650(45)	−3000	+3650
83	Bi	(+)1000(200)	−3550	+4550

[a] Includes the Lorentz term $-4\pi M_s/3 = -7$ kG.

volume overlap term to the measured hyperfine can often be quite meaningless; it should be compared to H_i. The H_i values obtained from Eqs. (2) and (3) can be considered in two categories, the *nsp* and *nd* impurities. In Sec. IV we show that the H_i values of the *nsp* impurities fit very well with a volume overlap calculation of the hff which uses a Hartree-Fock (HF) wave function which is modified to take into account the band nature of the Fe host.

A. *d*-CEP

There is now sufficient experimental data to see that a volume misfit term of the type of Eq. (1) does not work well for impurity atoms with d_i-like valence electrons, especially $3d$ electrons. Their measured hff values are too negative. This behavior is in agreement with the behavior of the moment perturbations seen surrounding *nd* impurities in Fe. These impurities were seen to perturb the host moments[29,33] by altering the d_i-like conduction-electron polarization (*d*-CEP) in a very systematic way in the vicinity of the impurity. This occurs because the d_i electrons are polarized by exchange interaction with the d_l electrons in much the same manner as the $4s$ conduction electrons. From analyzing the host hff,[29] saturation magnetization, and neutron scattering[33,34] data of dilute Fe alloys it was shown that the *d*-CEP in the region of the $3d$ impurity depends on the number, n_i, of d_i electrons of the impurity in the following way: at the beginning of the $3d$ series all the d electrons are loosely bound, so they are all itinerant. As the atomic number Z increases, some of the d electrons become more tightly bound as shown by the decrease in bandwidth in band-structure calculations.[35] It is well established from specific-heat data that all the d electrons of Cr are itinerant.[36] At Mn some of the d electrons become localized. However, as might be expected, Mn still has an appreciable number of itinerant d electrons and so exhibits antiferromagnetism. As Z increases further the degree of localization increases and the number of d_i electrons per atom decreases. Thus elements to the left of Fe have more d_i electrons than Fe while elements to the right of Fe have fewer d_i electrons than Fe. Elements of the $4d$ and $5d$ series show a similar behavior when in an Fe host. Upon alloying, each constituent tends to take on characteristics intermediate to its own elemental behavior and that of the other constituents (principle of accommodation). The *d*-CEP varies as a trigonometric function of $2k_F r$ so the first node occurs at $2k_F r$ equals a constant. Since $k_F \simeq n_i^{1/3}$, the position of the first node of the *d*-CEP curves depends on n_i. Thus an *nd* impurity atom in Fe changes n_i in its vicinity and consequentially affects the form of the *d*-CEP in its vicinity. Curve 2 of Fig. 3 is a pictorial representation of the *d*-CEP for pure Fe or for impurity atoms with no d electrons near the Fermi level, such as *nsp* atoms. A $3d$ element to the right of Fe in the Periodic Table has fewer d_i electrons than an Fe atom in pure Fe; so in its vicinity k_F decreases, causing the first node to be further out as depicted by curve 1 of Fig. 3. Thus the *d*-CEP is more positive in the region of the impurity atom as indicated in Fig. 3. In contrast, a $3d$ element to the left of Fe has more $3d_i$ electrons than Fe so k_F in its vicinity increases causing the first node to occur at a smaller distance than in pure Fe. Thus the *d*-CEP is more negative in the region near the impurity as indicated by curve 3 of Fig. 3. This is the behavior previously seen in the moment perturbations caused by these impurities.[29] Here we are concerned with the *nd* elements to the left of Fe that develop no moments. The negative *d*-CEP around such impurities causes a negative overlap polarization of the s electrons near the impurity and leads to H_i being negative for the $3d$ impurities. This effect will also tend

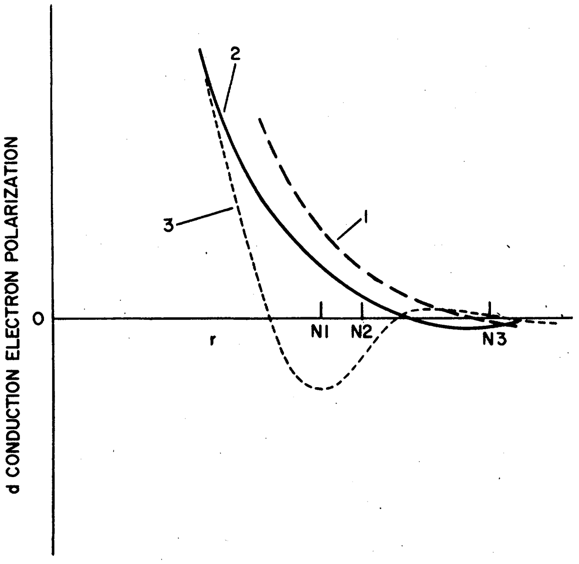

FIG. 3. Variation of the d-CEP as a function of distance in the vicinity of an nd impurity atom. 1 — — — fewer $3d_l$ electrons than Fe; 2 ——— pure Fe; 3 - - - - more $3d_l$ electrons than Fe.

to occur at the beginning of the $4d$ and $5d$ series. However, because the impurity $3d$ wave functions are more similar to those of the d electrons of Fe the effect will be largest for the $3d$ series and progressively less for the $4d$ and $5d$ impurities. That is, the increased number of nodes in the $4d$ and $5d$ series will tend to weaken this effect for these series. We see this in Table I where the H_i value of both Sc and Ti are negative while for the $4d$ series H_i for Y is negative but is positive for Zr. The H_i values of all the $5d$ nonmagnetic impurities are seen to have positive volume overlap terms. A quantitative estimate of this effect is very difficult, but we see that a version of the volume misfit model modified to take into account the distortion of the host d-CEP around the impurities atoms can qualitatively explain all the hff data for an Fe host.

The question arises as to why the difference in the polarization behavior of the conduction s and d_l electrons? That is, we have assumed that the impurity atoms have little affect on the s-CEP whereas impurities with d_l electrons strongly affect the d-CEP. The answer lies in the relative number and polarization interactions of the conduction s and d electrons. Fe has about one sp-like conduction electron per atom and ~ 0.2 d_l-like conduction electron per atom.[5,29] The sp-like electrons have little if any net polarization while the d_l electrons are about 90% polarized.[5,37] All impurity atoms have either one or two outer s electrons in the atomic state and they tend to contribute about one sp-like electron to the sp-conduction band of Fe. Thus the sp-conduction band is relatively unperturbed by the impurity. On the other hand the number of d_l-like conduction electrons varies widely, from 0 to 5 or more across a series. Thus, the relative change of conduction-electron density around impurities in Fe is much greater for d_l than s conduction electrons. Furthermore, the d_l-d_l exchange interaction (~ 1.5 eV) is much stronger than the s-d_l interaction, (~ 0.4 eV); consequently the relative change in the d-CEP will be much greater than that of the s-CEP of the host.

Several supposed difficulties[38] for the volume misfit model have been cited in the literature which we will now discuss:

1. *Volume overlap calculations*

Sondhi[28] calculated the volume overlap contribution for the $5sp$ series using atomic Hartree-Fock (HF), $\mathrm{Fe}^{+}(3d^{7})$ radical wave functions for Fe and concluded that it was an order of magnitude smaller than the measured value. It is well known that band d wave functions are more extended than atomic wave functions so we have calculated the H_i values using a modified HF wave function adjusted to have a radial distribution similar to that of an Fe band wave function. We have also included second and third nearest neighbors. The volume overlap contribution calculated in this way gives good agreement with the H_i values for both $4sp$ and $5sp$ impurity atoms. Details of this calculation are given in Sec. IV.

2. *hff pressure dependence*

The hff at Sn in Fe was observed[39] to become more negative as the pressure increased. The s-CEP term depends on the product $k_F r$ and thus, should not change with compression, since $k_F \sim 1/r$. If atoms were nondeformable, compressing the lattice would be expected to increase the overlap causing H_i and consequently H_Z to become more positive. However, the valence shells are deformable and Sn is more deformable than Fe, as indicated by the compressibility of Sn being about three times greater than that of Fe. Thus, upon compressing Sn in an Fe lattice, the Sn atom should compress more than the Fe atoms. Moreover, little is known about the way in which the wave functions are actually deformed. Thus much more would have to be understood about the behavior of the deformation to be sure what the pressure dependence means. It would also seem prudent to have data on more than one impurity before putting much trust in any interpretation of the pressure dependence.

3. *hff temperature dependences*

The temperature dependences of the hff at nonmagnetic impurities in Fe are very complicated and depend on many details of the behavior of both the *s* and *d* electronic and magnetic interactions with temperature. Thus so many unknown parameters enter such analyses that the credibility of any interpretations is in doubt at this time. Some of these complications have been discussed by Khoi *et al.*[40] Although that paper is quoted[38] as being at variance with the volume misfit model it actually analyzes the temperature dependence in terms of the transfer hff and thus, is very much in the spirit of this model.

4. *hff at impurities in Heusler alloys:* $X_2\mathrm{Mn}Y$

The Curie temperatures of the Heusler alloys are mainly dependent on the *X* atoms[41] with very little sensitivity to the *Z* atoms. Thus the Heusler alloys can be considered as "pseudo-Fe" in the sense that their ferromagnetism results from obtaining the correct combination of localized and itinerant *d* electrons to give ferromagnetism by combining elements to the left (Mn) and right (e.g., $X=\mathrm{Cu}$, Ni, Pd, or Pt) of Fe. Thus the magnetic behavior of these alloys is very similar to that of Fe.

It has been emphasized in the literature[6,38] that the *Y* site in Heusler alloys has only 2nn magnetic Mn neighbors and thus there should be too small an overlap to account for the observed hff values at the *Y* site. Actually both Sondhi's[28] and our calculation show that in Fe the 2nn has a larger overlap contribution than the 1nn for impurity from the first half of the 5*sp* shell. We have recently calculated[42] the hff variation at 5*sp* impurity atoms in the *Z* site in Heusler alloys and find that with *no* adjustable parameters relative to the Fe calculation the volume misfit model fits the measured values very satisfactorily.

III. HOST AND IMPURITY CONTRIBUTIONS NOT SEPARABLE: CHARGE-PERTURBATION MODELS

The many versions of the charge perturbation models have the common feature that they use scattering-theory formalism and incorporate the Friedel sum rule to determine the phase shifts.

A. Daniel and Friedel model

The original model is due to Daniel and Friedel.[1] In this model, as well as other versions of this type, the impurity atom was assumed to cause a charge perturbation proportional to ΔZ, the difference between the number of outer valence electrons of the impurity and the number of conduction electrons per host atom. There is some uncertainty, and therefore latitude, in how the latter quantity is defined for hosts which are alloys. The impurity atom was represented by a square well whose depth V_0 was determined by application of the Friedel sum rule

$$\Delta Z^{\pm}=\frac{1}{\pi}\sum_{l}(2l+1)\delta_l^{\pm} \ , \tag{4}$$

where δ_l is the phase shift at the Fermi energy. It should be noted that this procedure does not give well defined δ_l values since there is no consensus on how to apportion ΔZ between its various orbital components. An additional well depth proportional to a uniform spin polarization (ϵ) of the conduction electrons of the host was added or subtracted to V_0 depending on the spin of the scattering electrons. Since the conduction electrons scatter differently depending on their spin, a nonzero spin density occurs at the impurity. The hff at the origin was derived using the Fermi contact interaction. Jena and Geldart[7(a)] attempted to give a more rational interpretation to the approximations made in the Daniel-Friedel model and applied their model to the Heusler alloys.

The objection to such models is that they describe the impurity and host in very unrealistic terms. The electronic structure of the impurity is poorly represented by a square well and representing the *s*-CEP of the host by a uniform spin polarization is unjustified. An outstanding feature of the *s*-CEP is that it is oscillatory. The interpretation of the uniform polarization is thus very obscure; it can be seen that it *cannot* be interpreted as the net *s*-CEP from the following considerations: small impurity atoms with no charge perturbation, such as Cu and Au, have large negative hff values (−213 and −1500 kG, respectively). These arise from the summed *s*-CEP contributions of the oscillating *s*-CEP and depend on the position of the neighbor shells with respect to the oscillations. They do *not* depend on the sign of the *net s*-CEP. Both band calculations and experiments show that the net *s*-CEP is too small to give an appreciable hff. Thus, there is no uniform polarization and the sign of the net *s*-like polarization plays no role in the value of the hff. So ϵ appears to be an arbitrary parameter with no physical significance. Other inconsistencies in the interpretation of ϵ are discussed by Campbell in Ref. 41.

B. Blandin and Campbell model

A variation of this type of model which introduced the spin polarization in a more realistic manner was given by Blandin and Campbell[6] (BC). They represent the magnetic exchange interaction between the impurity and magnetic atoms by a spherical δ-function shell at the radius of the neighbor shells. The sign of this interaction was varied for the two spin directions. Under their assumptions, they obtained a spin density at the impurity of

$$p(r_n)\simeq J\cos(2k_F r_n+2\delta_0)/r_n^3 \ . \tag{5}$$

This is similar to an asymptotic RKKY-like variation with the addition of a phase shift $2\delta_0$, where, as usual, δ_0 is given by the Friedel sum rule. The hff is then obtained by using the Fermi contact interaction and summing over the near-neighbor shells. They interpret this model as an extension of the RKKY approach to an electron gas with a strong perturbation and apply it to impurities in both the Heusler alloys and pure Fe. In the application of this model BC add another term[6] of the form

$$\cos(2k_F r_n + \xi)/r_n^4 \ , \tag{6}$$

to represent the preasymptotic behavior where the phase shift is take to be $\xi \simeq \frac{1}{2}\pi$.

The hff is then given by

$$H_z = A_z \sum_n \left[\frac{A_n \cos(2k_F r_n + 2\delta_0)}{r_n^3} + \frac{B_n \cos(2k_F r_n + \xi)}{r_n^4} \right] . \tag{7}$$

In Fig. 4 we show a comparison of this model with the measured values of H_z divided by A_Z (of Ref. 4) for the Cu(4*sp*) and Ag(5*sp*) series in Fe. The five parameters used for this comparison are similar to those used by BC in Ref. 6 and are given in the caption of Fig. 4. The fit is seen to be poor; i.e., Eq. (7) gives a sinusoidal behavior which is not seen in the experimental data. The predicted BC model values of the hff in the Heusler alloy show the same type of sinusoidal behavior, leading to hff values that are too small compared to the measured values in the high ΔZ region. In the later version of this model[6] the k_F value for Heusler alloys was taken as that corresponding to the Y atom contributing only one electron to the conduction band, as is assumed in the volume overlap model.

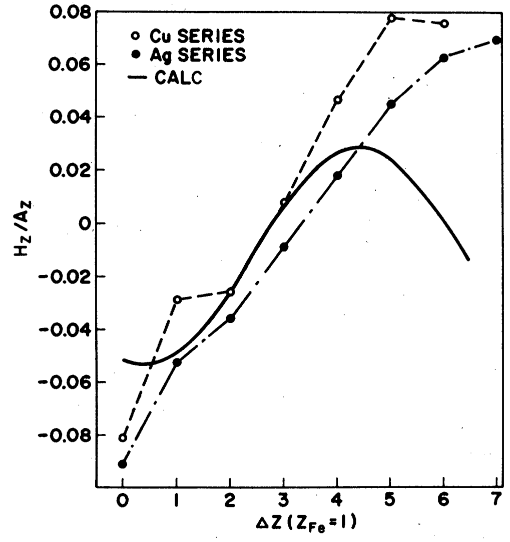

FIG. 4. Comparison of experimental values of H_z/A_z for 4*sp* and 5*sp* impurities in Fe and those calculated using the BC model (Ref. 6). A_z values are from Ref. 4. The parameters used in the calculating of the solid curve are $2k_F r_{\rm nn} = 5.63$, $\delta_0 = \delta_1 = \frac{1}{8}\Delta Z \pi$, $\xi = \frac{1}{2}\pi$, $A_{\rm nn} = -0.027 r_{\rm nn}^3$, and $B_{\rm nn} = -0.017 r_{\rm nn}^4$.

C. Caroli and Blandin model

Caroli and Blandin[2] proposed a different model in which the *s*-CEP resulted solely from interband mixing; i.e., $J_{\rm hyb}$. They used partial-wave-scattering analysis with only the $l = 2$ component being scattered. This model was developed to explain the hff at the X and Y atoms of the Heusler alloys $X_2{\rm Mn}Y$ where the moment of about $4\mu_B$ is located on the Mn atoms. Using the Friedel virtual level concept, five (spin up) of the six d electrons of Mn were assumed to be localized and have a phase shift of π. Applying the Friedel sum rule the other spin-down electron was given a phase shift of $\sim \frac{1}{5}\pi$. The *s*-like polarization was developed through hybridization. The difficulty with this model is that the polarization mainly depends on the host. The effect of the Y atoms enters only through their weak influence on k_F. Thus the original version predicted only negative hff values for all sites.

Jena and Geldart[7(b)] took into account the wave-vector dependence of the scattering and obtained a version which introduced additional amplitude and phase-shift parameters. This enabled them to remove the restriction that the phase shift depended only on the Mn atom and thus obtain a change in sign of the spin polarization surrounding the Mn atom. However, they have not applied this model to obtain hff values. It is incomplete since the polarization is due solely to the hybridization interaction.

In general all of the charge perturbation screening models give the hff in a modified form of the asymptotic scattering expression. In this way they introduce three or more parameters and attempt to fit the monotonically increasing hff values of the *nsp* impurities. The fits for an Fe host are very poor. The parameters are difficult to relate to physical quantities and the interpretations given of these parameters in the various models are often not consistent with known behaviors of these quantities.

IV. CALCULATION OF H_l

We show here that a reasonable modification of previous calculations of the transferred hff or volume overlap gives good agreement with the H_l values derived from the measured hff values for both 4*sp* and 5*sp* impurities in Fe. Following Shirley[3] and Sondhi[28] we use the model given by Watson and Freeman.[26] These previous calculations used atomic Hartree-Fock orbitals which are well known to be more localized than the orbitals in solids. Our calculations differ from those previously reported in mainly one respect. We have used an augmented Hartree-Fock atomic orbital for Fe which simulates the radial band orbital of Fe. For completeness we have also included contributions from all unshielded neighbors. For Fe this entails through third nearest neighbors. We find that, for $4sp$ and more so for $5sp$ impurities, contributions from the 2nn shells are appreciable.

A. Theory and details of calculation

The volume overlap contribution to the hyperfine fields observed at the nuclei of nonmagnetic solutes in ferromagnetic hosts has been discussed by several authors. However, for completeness we give a brief outline of the theory. Consider a wave function ψ constructed from one-electron orbitals of the type $\phi_{nm}(r_i)\alpha$, $\phi_{nm}(r_i)\beta$ for a solute–host-atom pair, where r_i is the space coordinate of the ith electron and α, β denote spin states. There is a contribution to the magnetic field at the solute atom from the overlap between the closed-shell s electrons of the solute and the $3d^{m=0}$ electrons of the host. Since this model only considers one impurity-host pair the $3d^{m=0}$ is the only d orbital of the host with a nonzero overlap with the ns orbitals of the impurity. This overlap leads to distortion of the solute orbitals which perturbs the electron density of the system. From first-order perturbation theory this results in a volume overlap contribution to the hyperfine field at the solute nucleus given by

$$H_v = \frac{8}{3}\pi\mu_B \sum_{n=1}^{n_0} \sum_{n'=1}^{n_0} S_n(r) S_{n'}(r) \phi_{ns}(0) \times \phi_{n's}(0) B_n^{1/2}(Z) B_{n'}^{1/2}(Z) \ , \qquad (8)$$

where $S_n(r)$ is the $3d$-ns overlap integral, $B_n^{1/2}(Z)$ is the relativistic correction factor,[43] μ_B is the Bohr magneton, $\phi_{ns}(0)$ is the value of the ns orbital at the solute nucleus, and n_0 is the number of doubly occupied s orbitals of the solute atom.

The overlap integral for a pair of atomic orbitals ϕ^a and ϕ^b of atoms a and b is defined for any internucleus distance r by

$$S(\phi^a, \phi^b, r) = \int \phi^{a*} \phi^b dv \ , \qquad (9)$$

where dv is the volume element and the integration is carried out over all space.

Shirley[3] used Eq. (8) to estimate the hyperfine field for Xe in a ferromagnetic host by considering only the contribution of the outer $5s$ orbital. Later, Sondhi[28] included the contribution of the inner shells and found the total field to be significantly smaller than Shirley's estimate. Both Shirley and Sondhi used Hartree-Fock (HF) atomic wave functions to calculate the overlap integrals $S_n(r)$.

We used the Hartree-Fock ground-state radial wave functions of Clementi and Roetti[44] (CR) for the s-orbital wave functions of the $4sp$ and $5sp$ atoms and the $3d$ orbital of Fe. Using the HF $Fe^+(3d^7)$ wave function we first compared the calculated overlaps obtained with the CR wave functions with those obtained by Sondhi who used Mann's[45] numerical HF wave functions. The two overlaps were in almost exact agreement. These values lead to the hff values listed in column 5 of Table IV. However, it is well known that the $3d$ HF orbitals of the $4s^2 3d^{n-2}$, $4s3d^{n-1}$, and $3d^n$ configurations of the transition metals can vary substantially between the isolated atom and the solid lattice.[46] The $3d$ Hartree-Fock orbital of the isolated atom is much more localized than the band orbital. To demonstrate this we show the radial probability density for the Fe d-like orbital of the HF ground-state wave function ($3d^7 4s$), labeled HF in Fig. 5, as compared to the radial probability density from the Fe band calculation of Duff and Das,[47] labeled DD. They found that the radial charge densities in the 100, 110, and 111 directions were very similar. We use an average. The radial dependences of the wave function at high-symmetry points at the Brillouin zone have often been given in the literature. In particular it has been pointed out[48] that higher energy bands (e.g., at H_{25}) are more localized than the lower (e.g., at H_{12}) energy bands. This can be misleading since it is not an accurate representation of the band wave functions. For this an average should be taken over k space as was done by DD and is shown in Fig. 5. Note that although both the HF

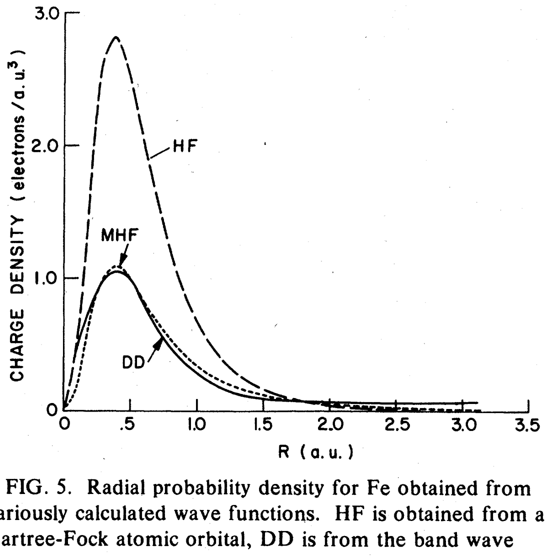

FIG. 5. Radial probability density for Fe obtained from variously calculated wave functions. HF is obtained from a Hartree-Fock atomic orbital, DD is from the band wave function calculated by Duff and Das, and MHF is from a modified bandlike Hartree-Fock orbital as discussed in the text. The radial distance is given in atomic units.

and DD distributions have their maximum probabilities at approximately the same position, $R = 0.4$ a.u., the Hartree-Fock orbital is significantly more localized. In order to approximate the band orbital more closely we modified the Hartree-Fock $3d$ orbital given by Clementi and Roetti in the following way: The orbital was initially a five component Slater orbital expansion of near Hartree-Fock quality. The coefficients and exponents of CR are given in column 2 of Table II. To make the orbital more diffuse a sixth component was added with an exponential scale of $\alpha_i = 1.0$. The use of the exponent $\alpha_i = 1$ is not excessive but in keeping with similar exponents which were used to optimize the energy levels of Fe in a solid.[46] The relative coefficient of this diffuse component was varied so that the radial probability density of the modified HF function agreed with the DD band orbital at $R = 0.5$ a.u. The probability density of this modified HF orbital is shown as MHF in Fig. 5 and is seen to rather closely simulate the distribution of the DD band orbital. All these orbitals have been normalized to contain one electron. As seen in Fig. 5 our MHF orbital is somewhat smaller than the DD band orbital in the interatomic region beyond 2 a.u. This is as it should be since the DD orbital is normalized to unity for each unit cell. Thus in the band calculation the overlap contributions of the nearest neighbors increases the electron density in the interatomic region. However, at $R = 0.5$ a.u. the contribution to the radial probability density from nearest neighbors is negligible. Thus, we modified the HF orbital to agree in that region. Admittedly, this is a somewhat arbitrary procedure since the DD band orbital contains about 12% sp character while our MHF is of pure d-like character. Nevertheless, this procedure seems to be a reasonable first approximation; similar additions to the basis set have been made in many past calculations and have been shown to be justifiable.[46,48] The renormalized coefficients for the MHF orbital are listed in column 3 of Table II. We then used this MHF radial orbital to calculate the overlap integrals $S_n(r)$.

TABLE II. $3d$ orbitals for Fe of the form $\phi = \Sigma C_i \chi_i$ where $\chi_i = N_i r^2 e^{-\alpha_i r}$ and $N_i = (6!)^{-1/2}(2\alpha_i)^{7/2}$.

	Hartree-Fock orbital[a]	Modified Hartree-Fock orbital
α_i	C_i	C_i
11.543 90	0.026 01	0.015 84
6.188 54	0.236 79	0.144 16
4.025 12	0.279 92	0.170 42
2.620 70	0.387 59	0.235 97
1.412 67	0.265 99	0.161 94
1.000 00	- - -	0.547 94

[a]Reference 44: ^5F-$4s^1 3d^7$ state of Fe.

Some points concerning the addition of the diffuse component to the HF basis should be made clear. Since we are fitting a probability density by considering only one point ($R = 0.5$ a.u.), the value used for the exponential scale factor is not critical. That is, if a more diffuse function were used (e.g., $\alpha = 0.8$) the relative coefficient of the diffuse component would just become smaller. A series of calculations to determine the sensitivity of the results to variations in α was not attempted. α should be considered an empirical parameter and a sensitivity study would probably not be meaningful unless the optimization was determined in some variational way; for example by calculating the energy of the system. In addition the basis functions used to describe the s electrons of the impurity atom were kept at the HF value. It is not unreasonable to expect these functions to be changed by the presence of the host. This would also affect the value of α. Improvements, of this nature, would require a significantly more detailed calculation than attempted here. The significant point is that with this one change in the basis set we can describe the entire $4sp$ and $5sp$ series.

Since we are dealing with a very dilute system, each solute atom can be considered to be completely surrounded by Fe atoms. Thus the solute atom can clearly "see" each Fe atom in the first three-neighbor shells (see Fig. 6). If we assume pairwise additivity for each of these three shells, H_v is given by

$$H_v = 8H_v^1 + 6H_v^2 + 12H_v^3 \ , \tag{10}$$

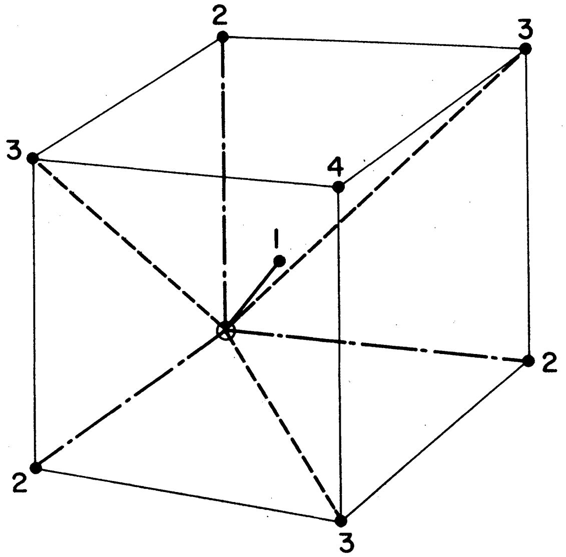

FIG. 6. Schematic of impurities "view" of first, second, third, and fourth nearest iron neighbors.

where the superscript indicates 1nn, 2nn, and 3nn shells and the coefficients are the number of sites in that shell. In Sec. IV B it will be seen that the 2nn and 3nn should not be omitted.

We also took into account the expansion of the lattice due to the presence of the impurity atom in the following manner: From a detailed cluster calculation Drientje and Ekster[49] obtained the lattice relaxation of the first and second neighbors of a Xe atom in Fe. The 1nn and 2nn Fe atoms were found to move out from their positions in pure Fe by 0.23 and 0.10 Å, respectively. The 3nn Fe atoms were assumed to be unchanged. The changes for the other solutes were obtained by

$$\delta_Z = \delta_{\mathrm{Xe}} \frac{V_Z^{1/3} - V_{\mathrm{Fe}}^{1/3}}{V_{\mathrm{Xe}}^{1/3} - V_{\mathrm{Fe}}^{1/3}} , \qquad (11)$$

where δ_Z is the position change and V_Z is the atomic volume of solute Z. This modification is minor and slightly decreases the overlap contribution.

The hff given by Eq. (8) represents that resulting from one $3d$ orbital. So we need a further factor to take into account that the Fe has a moment of 2.2 unpaired spin states. Since band calculations have confirmed the usual assumption[50] that the occupied part of the d band has all m quantum numbers fairly equally populated we take the factor to be $n_d = 2.2/5$. The total calculated transferred hff is thus

$$H_v^{\mathrm{tot}} = n_d H_d \ .$$

To reliably evaluate the $5sp$ series we found it necessary to set all overlaps integrals involving $1s$ or $2s$ orbitals which were less than 1×10^{-4} equal to zero. This was to avoid problems which resulted from taking the difference of the sums of products of small overlaps, $S_n(r)$, with corresponding large $\phi_{ns}(0)$ values. This was not necessary for the $4sp$ series. This procedure caused changes in some H_v values by as much as 25%, but eliminated spurious computational fluctuations across the row. This problem has been noted by others[46, 51] and will be particularly troublesome if more detailed calculations of this type are attempted.

The A_Z values are needed to obtain the s-CEP contribution H from Eq. (8). These are given by

$$A_Z = \tfrac{8}{3} \pi \mu_{\mathrm{B}} |\phi_{4s,5s}(0)|^2 \ . \qquad (12)$$

Since only the ratios of A_Z / A_{Fe} enter in calculating H_h^Z we want a consistent set of values. Thus we used CR wave functions for all atoms. We list the values obtained in column 2 of Table III. Previous calculated values are also listed in Table III. Campbell's[4] values were obtained from relativistic numerical formula. The Watson and Bennett[30] values were obtained from relativistic numerical HF wave functions. As can be seen from Table III our numbers are consistently smaller than Watson and Bennett's by almost a constant factor. The nature of this difference appears to be that they adjusted their calculated values to fit the known experimental values.[20] For consistency we use the hyperfine coupling constants derived from the same basis set as used for the core electrons. Thus we use our A_Z values. Since only the ratios A_Z / A_{Fe} enter in calculating the s-CEP contribution [see Eq. (3)], the H_i values derived from experiment are essentially independent of the basis set used.

TABLE III. Free-atom valence-s-electron hyperfine-coupling constants, $A(Z)$. Units of MG.

Z		This work	Campbell[a]	Watson[b] and Bennett
26	Fe	1.46	1.78	1.95
30	Zn	2.6	3.5	3.9
31	Ga	4.05	4.5	6.2
32	Ge	5.6	5.7	- - -
33	As	7.4	7.1	10.9
34	Se	9.4	8.7	14
35	Br	11.7	10.9	- - -
36	Kr	14.2	13.0	- - -
48	Cd	4.7	6.5	7.2
49	In	6.8	8.2	10
50	Sn	9.0	10.1	13
51	Sb	11.3	12.8	16
52	Te	13.9	15	21
53	I	16.8	18	23
54	Xe	19.9	22	- - -

[a] Reference 4. [b] Reference 30.

B. Comparison of calculated and experimental values

The experimental values of the impurity contribution, H_i, were obtained using Eqs. (2) and (3) and are listed in column 4 of Table IV. We have also listed the measured values H_Z and H_h in columns 2 and 3, respectively. Note that the H_h values are large and negative resulting in H_i being very different from H_Z. Thus it is only meaningful to compare H_v to H_i but not to the measured hff value as is often done. We list our calculated H_v^{tot} values in column 6 of Table IV. The values obtained from HF wave functions are listed in column 5. They all seem to be about a factor of 10 smaller than those calculated with MHF wave functions. The various subshell contributions are listed in Table V. It can be seen that the overlap contribution from the 2nn is often considerable. In fact the 2nn shell is of such a magnitude that the fields at the nsp atoms in Heusler alloys are also in agreement with that obtained from the volume misfit

TABLE IV. Comparison of experimental and calculated hyperfine-field contributions.

	H_Z^{a}	H_h	H_i (expt)	H_v^{tot} (HF)	H_v^{tot} (MHF)
Zn	−102(15)	−270	170	20	140
Ga	(−)117(3)	−415	300	50	455
Ge	46(5)	−580	625	100	860
As	333	−760	1090	140	1290
Se	680(50)	−970	1650	160	1630
Br	830(120)	−1200	2030	160	1910
Kr	- - -	−1460	- - -	170	2050
Cd	−347(2)	−480	135	15	200
In	−295(6)	−700	405	60	630
Sn	−88(3)	−920	830	110	930
Sb	227(5)	−1160	1390	160	1210
Te	670(4)	−1430	2100	220	2220
I	1137(2)	−1725	2860	270	2810
Xe	1540(100)	−2050	3590	280	3200

[a] These values include the Lorentz term $-\frac{4}{3}\pi M_s = -7\text{kG}$.

model.[42] We compare the experimental H_i values and calculated H_v^{tot} values in Fig. 7. We see in Fig. 7 that the agreement between the experimental impurity atom contribution and the calculated value H_v^{tot} is remarkably good for both 4*sp* and 5*sp* impurities all the way across each series. Note that even the somewhat different slopes of the two series are obtained correctly with the MHF wave function. This behavior has not been obtained with any other model.

The procedure used here to modify the HF orbital to be more representative of the *d* orbitals in the solid state is admittedly a rough approximation. These calculations could be improved by using the actual *d* orbitals obtained from a band calculation. This would give a more accurate representation of the localized and itinerant character of the *d* orbitals.

TABLE V. Subshell volume-overlap impurity hyperfine-field contribution using the MHF Fe orbitals.

	H_1 (kG)	H_2 (kG)	H_3 (kG)
Zn	2	46	94
Ga	170	160	130
Ge	415	290	150
As	710	420	160
Se	950	520	160
Br	1155	600	150
Kr	1320	660	65
Cd	1	2	201
In	87	240	300
Sn	350	230	340
Sb	430	415	365
Te	770	1055	395
I	1155	1245	410
Xe	1420	1370	410

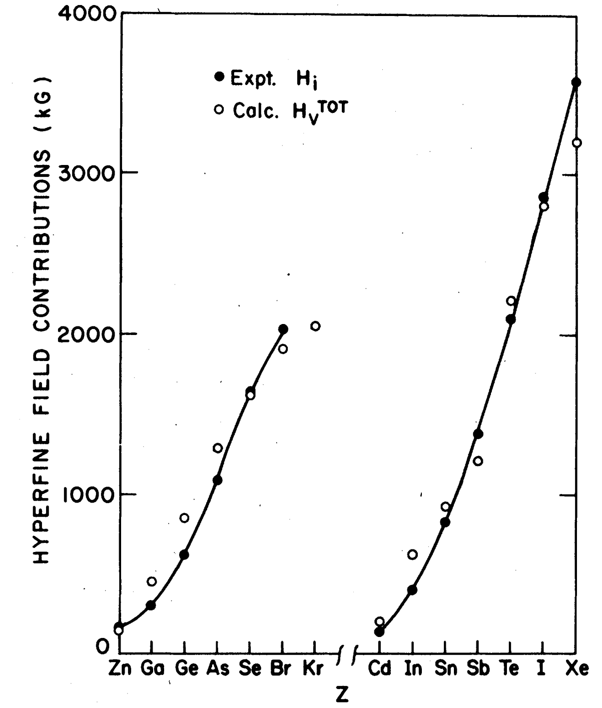

FIG. 7. Experimentally determined and calculated volume-overlap hyperfine-field contributions for 4*sp* and 5*sp* solutes in Fe. It is found that all three shells should be included.

A further improvement would be to include covalent or hybridization effects between solute and host. To do this in a reliable fashion would require variational calculations which are much sophisticated and difficult than that presented here.

V. SUMMARY AND CONCLUSIONS

The underlying assumptions and comparisons of the two types of models used to describe the hyperfine fields at nonmagnetic impurity atoms are:

A. Nonseparable model

(i) All the *sp* valence electrons of the impurity are assumed to become conduction electrons leading to the *s*-CEP being highly perturbed. (ii) The scattering-theory formalism is used to calculate the highly perturbed *s*-CEP. (iii) It is difficult to relate the parameters used in these analyses to other measured or calculated quantities. (iv) Some models consider only one of the *s*-CEP contributions, $J_{\rm dir}$ or $J_{\rm hyb}$. Both must be included since they are about equally important.

B. Separable model

(i) The *sp* impurities contribute only about the same number of *sp*-like conduction electrons which are characteristic of the host. Thus the *s*-CEP of the host is assumed to be unperturbed by the impurity atom. (ii) The hff contribution due to the impurity atom is given by the transferred hff or volume overlap with the host atoms. (iii) The quantities entering the analysis are directly related to other measured or calculated properties of the host and impurity atoms. (iv) The experimentally determined host *s*-CEP is used so it is assured of containing both exchange interactions, $J_{\rm dir}$ and $J_{\rm hyb}$, correctly.

The behavior of the hyperfine fields at the nonmagnetic *nd* impurities can be qualitatively understood in terms of the *d*-CEP in the vicinity of the impurity atom.

We have shown that the volume-overlap misfit model can give a good description of the hyperfine fields at nonmagnetic 4*sp* and 5*sp* impurities in Fe if the basis functions of the *d* orbitals are expanded to be more representative of Fe atoms in a solid.

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