Origin of the Hyperfine Fields in Pure Fe and at Solute Atoms in Fe

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The measured spin-density oscillations in Fe (preceding paper) are interpreted as due to 4s-like conduction-electron polarization and compared with improved Ruderman-Kittel-Kasuya-Yosida-type calculations. The hyperfine field shifts due to a solute atom are shown to be due to moment perturbations rather than charge perturbations, and agreement with the improved RKKY-type calculations is considered to be quite good. We find $J_{\text{int}}(q=0) \sim +0.5$ eV. There is some indication that the exchange interaction and interband mixing cause comparable polarizations in the region of the nearest-neighbor shell. We find the net integrated 4s-like polarization in pure Fe to be about +(5–8)%. Using the latest Fe band calculations, we are able to obtain identifications and magnitudes for the terms contributing to the hyperfine field of Fe. With this model we are able to explain the well-known variations of hyperfine fields at solute atoms in Fe. There is shown to be a positive hyperfine field contribution from the polarization induced in the ns-like electron density near the solute atom. This positive polarization is proportional to the volume overlap of the solute atom with the Fe matrix.

I. INTRODUCTION

Ferromagnetism in metals is believed to be achieved by the "local" atomic moments being aligned through the intermediary of the polarized "itinerant" electrons.[1] Many experiments and calculations have been carried out in recent years to investigate this interaction. Two aspects of the interaction have now been considered in some detail: the s-$d(f)$ indirect exchange coupling and interband mixing. The first is the RKKY- (Ruderman, Kittel, Kasuya, and Yosida) type interaction[1] where the spin density of the itinerant electrons arises from a Coulomb exchange interaction $J_{\text{int}}(\vec{k}, \vec{k}')$ between the localized and itinerant electrons. This always yields a net conduction-electron polarization (CEP) of spin parallel to that of the local moments, i.e., $J_{\text{int}}(q=0)>0$. In recent years most of the effort in these calculations has been oriented toward improving the original approximations in the RKKY theory. The following approximations have been investigated: (a) the k dependence of the Bloch wave functions,[2,3] (b) the q approximation,[3] i.e., $J_{\text{int}}(\vec{k}, \vec{k}')=J_{\text{int}}(q=\vec{k}-\vec{k}')$, (c) effect of an interacting electron gas,[2,3(b)4,5] and (d) nonspherical Fermi surface.[6] The second type of mechanism considered, an effective exchange interaction J' through interband mixing[3(a)7,8] of the conduction and local-moment electron orbitals, leads under most conditions to a negative CEP. In general, both these terms contribute to the interaction, so $J_{\text{eff}}(q=0)=J_{\text{int}}+J'$ could have either sign.

Information on the value of $J_{\text{eff}}(q=0)$ is obtained from many types of experiments. Spin-disorder magnetic resistance, resistance anomalies, superconducting transition temperatures, and paramagnetic Curie temperatures yield values for the rare earths[9] of $|J_{\text{eff}}(0)| \sim |0.1$ eV. For dilute alloys of Mn in nontransition metals, values of $J_{\text{eff}}(0)$ vary from about 0.2 to 1 eV depending on the type experiment. Nuclear magnetic resonance[10] Knight-shift measurements and electron spin resonance[11] give values of $J_{\text{eff}}(0)$ for rare earths in alloys and intermetallic compounds which are often negative and in the range of -0.02 to -0.25 eV. The negative values are interpreted to indicate that for these cases the interband mixing dominates. Line broadening has indicated that the effective CEP range in Pd alloys is an order of magnitude larger than that predicted by the free-electron model. Information about the spin-density distribution has been obtained from neutron scattering measurements[12] of the magnetic form factors in dilute alloys. But by far the most detailed information on the spin density can be obtained by hyperfine field measurements with Mössbauer[13,14] and NMR[15–17] experiments. This gives a direct measure of the spin polarization $\rho(R)$ which is closely related to $J(\vec{k}, \vec{k}')$.

It should be emphasized that the results of the various types of experiments are not necessarily comparable, but different aspects and averages of $J(\vec{k}, \vec{k}')$ are obtained from different experiments. Care must be taken to realize what feature each experiment is emphasizing. For example, the EPR g shifts measure $J_{\text{eff}}(0)$ only and weight strongly the portions of $J(\vec{k}, \vec{k}')$ with symmetries like the local-moment orbitals; the neutron experiments measure the total spin form factor due to both local and *all* itinerant electrons; the hyperfine field measurements on transition elements where the orbital moments are quenched, essentially see only the s-like portions of $J(\vec{k}, \vec{k}')$.

In the preceding paper[18] hereafter referred to as Paper I we reported on the measurements of the variations in hyperfine fields with alloying in ordered *Fe*Si alloys. By combining these measurements

with dilute-*Fe* Si-alloy data[13,15] we obtained values for the percentage shifts for the various neighbor shells in pure Fe (see Table VI and Fig. 8 in I). We interpret these shifts as due to s-like conduction-electron polarization (CEP) which is closely related to $J_{eff}(\vec{k}, \vec{k}')$. In Sec. II we use the latest Fe band calculations[19] and obtain the self-polarization contribution to the hyperfine field H_s. A comparison with improved RKKY and charge-density oscillation theories is made in Secs. III and IV. Having thus obtained the hyperfine field contribution from Fe neighbors we can understand and interpret the observed variation of the hyperfine field at solute atoms in Fe. This is done in Sec. V, where we find a positive contribution at the solute atom from a volume misfit effect. Finally in Sec. VI using the present model we discuss the variation of the hyperfine field at a given type configuration site with alloying. This is believed to be related to the changes in hyperfine field with volume (or pressure) changes. It is shown to depend on many more quantities than the hyperfine field constant and saturation magnetization as is usually assumed.

II. COMPARISON WITH BAND CALCULATIONS

For transition metals where the orbital angular momentum is quenched, the internal field at a particular atom can be thought of as arising from a core polarization H_c and a 4s-like CEP contribution, i.e., $H_{Fe}=H_{cp}+H_{ce}$. The CEP contribution can be further considered as due to the sum of two terms: one due to self-polarization of the s-like conduction electrons by the atom itself, H_s, the other due to the sum of the CEP effects from all the neighbors, H_Σ. Thus

$$H_{Fe}=H_{cp}+H_s+H_\Sigma \tag{1}$$

We know $H_{Fe}=-340$ kG and H_Σ may be obtained by summing the shifts in column 5 of Table VI in I over the first 6nn shells weighted by the number of atoms in each neighbor shell assuming that contributions from the higher shells essentially cancel out. We thus obtain $H_\Sigma \simeq -145$ kG. We will now evaluate H_{cp} and thus H_s in two ways: The first is essentially a free-atom model and uses only experimental data for H_{cp}. It gives limiting values for both H_{cp} and H_s. The second uses the value of H_{cp} from the latest band calculations of ferromagnetic Fe and gives the best estimate of H_S. The magnetic moments and hyperfine fields for Fe atoms in a number of nonmetallic compounds[20] have been measured and the hyperfine field per Bohr magneton is remarkably constant with a value of about $-(110-120)$ kG/μ_B. It therefore appears that the core contribution in nonmetallics is quite insensitive to the environment and type of bonding of the Fe atom. If it had a similar value in the Fe metallic state, we would obtain $H_{cp}\sim -250$ kG. This leads to a value for H_s of about +55 kG. We consider these the highest and lowest values, respectively, for these quantities. The values for the three contributions to the hyperfine field are listed in Table I.

We list in Table II the calculated values of the hyperfine fields due to core electrons (1s through 3p) and band electrons (3d, 4s, 4p) for various band calculations.[19,21,22] The values given for H_{ce} are equivalent to the weighted average of the CEP curve, i.e., H_s+H_Σ. Using a value of $H_{cp}(-400$ kG) from the latest calculation of Duff and Das[19] (DD) which incorporated the experience of the previous calculation, we obtain $H_s \simeq +205$ kG. These values are listed in Table I. We expect the core contribution in the metallic state to be more negative than the atomic value for two reasons. The 3d wave functions in metallic Fe are presumably more extended than the atomic 3d wave functions. Thus the s-d exchange interaction attracts the spin-up 4s electrons to larger radii leaving more 4s spin-down electrons at the origin, making the internal field more negative. The second effect is the hybridization of the 3d-4s electrons. This also gives a negative contribution,[7] as seen in Table II. We have listed in the last column of Table I the values of H_{ce} obtained from the two evaluations of H_{cp} and H_s. We see that using the atomic H_{cp} yields a value of -90 kG and using the band calculation H_{cp} yields + 60 kG for H_{ce}. The former seems to be too negative while the latter (+ 60 kG) is quite reasonable and is consistent with the band calculation which gives + 33 kG for H_{ce}. We thus obtain the value for the percentage shift at the origin of 60 [= (205/340)×100]. The ratio between the percentage shift at the origin and the 1nn value is thus around seven or eight.

III. COMPARISON WITH SPIN-DENSITY CALCULATIONS OF THE RKKY-TYPE INTERBAND MIXING

Since an Fe atom in an Fe lattice has both a charge and spin, substituting in a Si atom should give rise to both charge- and spin-density oscillations. In a ferromagnetic material the charge-density oscillation will also give rise to a spin-density oscillation.[23] In the usual linear approximation the two effects are separable. Let us first consider the spin-density oscillation due to the Fe moment. (We shall see in Sec. IV that the spin oscillation resulting from the

TABLE I. Values of the contributions to the hyperfine field of Fe.

	H_Σ (kG)	H_{cp}(kG)	H_s (kG)	H_{ce} (kG) = $H_s + H_\Sigma$
"Free-atom"	−145	−250	+ 55	−90
Band calc (DD)	−145	−400	+ 205	+ 60

TABLE II. Hyperfine-field contributions from band calculations.

	H_{cp} (kG)	H_{ce} (kG)
Atomiclike + s-d exchange (Watson and Freeman) [a]		
$3d^6 4s^2$	−320	+195
$3d^8$	−350	
Atomiclike + s-d exchange + hybridization		
Wakoh and Yamashita (WY) [b]	−355	−52
Duff and Das (DD) [c]	−400	+33

[a]Reference 21.
[b]Reference 22.
[c]Reference 19(b).

charge perturbation is an order of magnitude smaller than that due to the moment perturbation.) The spin-density oscillation is directly related to the exchange integral by (see Ref. 3)

$$\Delta\rho(\vec{R}) \sim -S \sum_{\vec{k}=0}^{\vec{k}_F} \sum_{\vec{k}'=0}^{\infty} \frac{J_{\text{eff}}(\vec{k},\vec{k}')}{\epsilon_{\vec{k}} - \epsilon_{\vec{k}'}} \times \left| \varphi^*_{\vec{k}}(\vec{R})\varphi_{\vec{k}'}(\vec{R}) + \varphi_{\vec{k}}(\vec{R})\varphi^*_{\vec{k}'}(\vec{R}) \right| , \quad (2)$$

where S is the local-moment spin operator, and $\epsilon_{\vec{k}}$ and $\varphi_{\vec{k}}$ are the energy and wave functions of the conduction electrons of wave vector $\vec{k}$. In the RKKY approximation, $J_{\text{eff}}(\vec{k},\vec{k}')$ is equal to the exchange integral $J_{\text{int}}(q)$, the q approximation is made, and plane waves are used for the electrons. Furthermore $J_{\text{int}}(q)$ is taken equal to a constant. This leads to the well-known RKKY formula[1]

$$\frac{\Delta\rho}{\rho}(R) = -\frac{9\pi n}{E_F} J_{\text{int}}(0) S \times \frac{2k_F R\cos(2k_F R) - \sin(2k_F R)}{(2k_F R)^4} , \quad (3)$$

where n is the number of 4s conduction electrons per atom and S is the spin of the magnetic ion (~1). Equation (3) is shown as the dashed curve in Fig. 1 for $E_F = 5$ eV, $k_F = 1.3\times10^8$ cm^{-1} (giving $n = 0.8$ electrons/atom), and $J_{\text{int}}(0) = +0.9$ eV. These are very reasonable values for k_F and $J_{\text{int}}(0)$. In order to obtain these values we have adjusted the RKKY curve to go through the first- and second-neighbor points. Note that the fit is quite poor in the region 3–5nn shells. The measured curve tends to stay positive rather than have a second negative oscillation in this region. We can compare the value of $J_{\text{int}}(0)$ to those of the s band splitting at the Γ point. WK[22] obtained 0.5 eV and DD[19] obtained 1.4 eV. However, the band calculation indicated that hybridization was appreciable,[19(b)] so we expect the CEP to also have a considerable contribution from interband mixing. Thus the RKKY amplitude should be smaller. A value for $J_{\text{int}}(0)$ of about 0.5 eV is probably more reasonable.

As mentioned in the Introduction, the various approximations made in evaluating Eq. (2) have been investigated in some detail. Although Eq. (3) becomes infinite at the origin because $J(q)$ was assumed to be constant for all q, its behavior from half a lattice distance on out fits the data as well as the improved calculations. Introducing a falloff for $J(q)$ at large q keeps the value $\Delta\rho(0)$ finite. Kaplan[2] used orthogonalized plane waves (OPW) for the conduction electrons and the form factor approximation[24] for $J_{\text{int}}(q)$. This gives a polarization at the origin which is about eight times larger than is estimated from experiment but shows little difference from Eq. (3) for values of R greater than 0.3.

Calculations of $\Delta\rho(R)$ investigating the q approximation (using OPW's but still without interband mixing) seem to show fair agreement with experiment.[3(c)] For example, for $k_F \sim 1.9\times10^8$ cm^{-1} the amplitude of the first oscillation has about the correct polarization and occurs at about $R = 1$ [see Fig. 3 of Ref. 3(c)]. Again, however, the value at the origin is about six times larger than that estimated from experiment and band calculations.

The effect of interband mixing was investigated in Refs. 3(a) and 3(d). This effect was investigated only for a S-state Gd $4f^7$ local moment. The

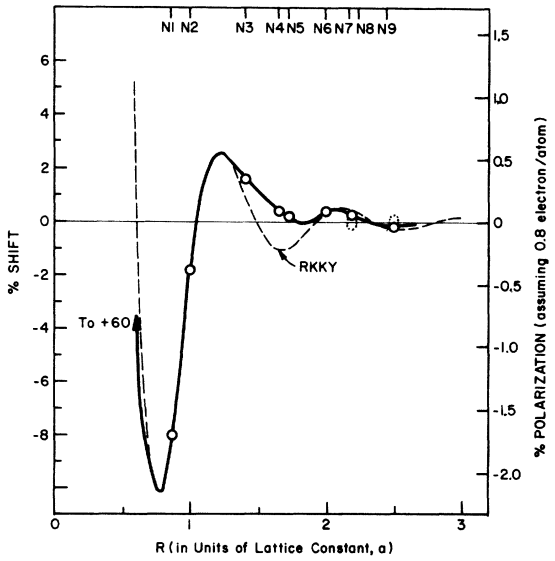

FIG. 1. Extrapolated percentage hyperfine field shifts for each neighbor shell in pure Fe as a function of the distance of that shell from the origin (Ref. 18) (solid curve). These shifts are interpreted to be a measure of the variation of the spin polarization of the 4s-like electrons with distance from a Fe atom. The dashed curve shows the RKKY approximation for $k_F = 1.28\times10^8$ cm^{-1} and $J_{\text{int}}(q=0) = 0.9$ eV.

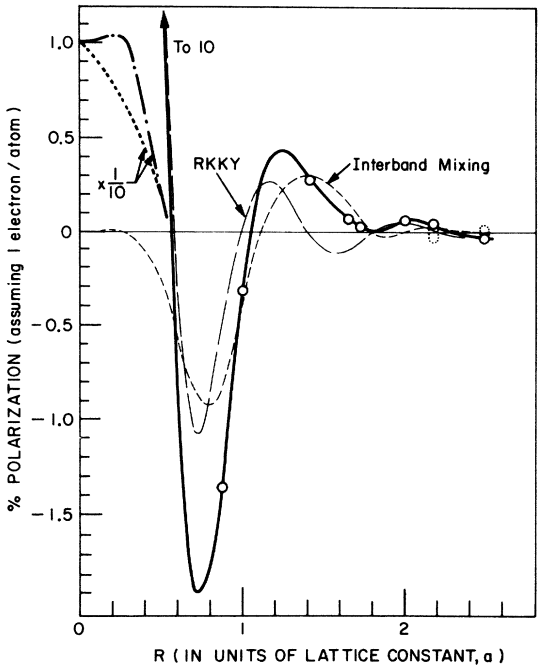

FIG. 2. Proposed decomposition of experimentally measured polarization curve (solid) into exchange (long dashed) and interband mixing (short dashed) contributions.

results indicated that the main peak was more diffuse and the phase of the oscillations is shifted outward with respect to those associated with $J_{\rm int}$. Assuming that the exchange and interband mixing contributions are comparable at the nearest-neighbor distance, we estimate the form of the interband mixing from the experimental data by subtracting the RKKY-type exchange contribution from the measured CEP curve. However, we must emphasize at this point that this procedure may assume entirely too much credibility for the form of the exchange contribution and the interpretation of the experimental data since many approximations are involved in both of these results. Also, electron-electron correlations, which may alter the interpretations considerably, have been entirely neglected. But with these qualifications, as shown in Fig. 2, we subtract an RKKY-type curve (long dashed), derived from Eq. (3) with $k_F = 1.35 \times 10^8$ cm^{-1} ($n = 1$ electron/atom) and $J_{\rm int}(0) = 0.5$ eV, from the experimental curve (solid). The polarization scale shown here also corresponds to $n = 1$. We obtain the short dashed curve which indeed has the features described in Ref. 3(d) by Watson *et al.* for interband mixing. That is, it is more diffuse and the phase of the oscillations is shifted outward with respect to the RKKY curve. Thus the lack of a second negative oscillation around $R = 1.5$ may be due to interference of the two contributions—in fact one would expect distortions of this type to occur in the net polarization curve. On the other hand an interband mixing contribution is expected to be anisotropic giving rise to anisotropies in the CEP curve. No such effects are observed. An interband contribution to the CEP comparable to that of exchange would lead to a calculated value at the origin which is about a factor two less than before. This reduces the discrepancy of the ratio of the theoretical to the experimental value estimated at the origin above to a factor of 3–4.

The effect of exchange enhancement of the type $\chi_0/(1+\beta\chi_0)$ (where χ_0 is the noninteracting-electron-gas spin susceptibility and β a measure of the strength of the conduction-electron-conduction-electron exchange interaction) has been investigated many times [3(b),4,5] and shown to make the spin density progressively more positive toward the origin. This is the opposite type of behavior needed to improve agreement between any theoretical calculations and experiment. An electron-gas susceptibility function with a bump at $q = 2k_F$ due to the effects of conduction-electron interactions[5,13(c)] could easily account for the discrepancy of a factor of 3 or 4 at the origin. However the theoretical calculations do show clearly that the region near the origin is somewhat sensitive to the wave functions and approximations used; beyond $R = 0.5a$ the various approximations have little effect on the shape of the $\Delta\sigma(R)$ curve. Thus a discrepancy of a factor of 3 or 4 at the origin may well be within the accuracy of theory and experiment at this time.

We can obtain the net polarization of the 4*s* conduction band (as opposed to the lattice weighted) by integrating the polarization curve. For this we have assumed two rather extreme polarization behaviors near the origin as shown by the dot-dashed or dotted curves in Fig. 2. The integral is quite insensitive to this exact behavior at the origin since the CEP curve is multiplied by R^2 to obtain the integral. We find a net polarization of + (5–8)%. The band calculation of WY[22] gave – 2% for the quantity. However, DD[19] have questioned this feature of the WY calculation and would favor a net polarization of about the same magnitude but of positive sign. Although an early interpretation of neutron magnetic scattering on Fe suggested negative polarization of the 4*s* band, it is now realized that such an interpretation is not necessary.[19(b),25] Neutron scattering experiments measure the integral of the *total* spin-density curve not just a weighted average of the 4*s* polarization at the lattice sites as measured in hyperfine field measurements.

As has been pointed out before,[5,13] the strong negative oscillation at nearest neighbors means that the 4*s*-like electrons would tend to produce antiferromagnetism in Fe, so the ferromagnetism must be due to positively polarized itinerant 3*d*-like electrons.

IV. ESTIMATION OF SPIN-DENSITY OSCILLATIONS DUE TO CHARGE PERTURBATIONS

In the previous discussion we have assumed that the observed polarization is due to the moment perturbations caused by replacing an Fe atom with an impurity atom of zero moment. However, in actuality a charge perturbation also exists. In the ordered alloy experiments a Si atom was replaced by an Fe atom and in the dilute alloys an Fe is replaced by a Si or other impurity atom. Daniel and Friedel[23] have proposed a mechanism which produces a spin-density change due to a charge perturbation in ferromagnetic metals. They proposed that the impurity atom has different perturbation potentials for spin-up and spin-down conduction electrons because of the splitting of these bands in ferromagnetic metals. They then argued that because of the suppression of the s-d exchange interaction in the impurity cell the spin-up electrons are less attracted to this region than the spin-down electrons. This leads to a negative hyperfine field at the impurity atom. They claimed that this effect should decrease as the charge difference of the host atom and impurity atom, ΔZ, increases because the perturbation potentials become more nearly the same depth for larger ΔZ. Thus they found that the hyperfine field should be about a factor of 2 smaller for $\Delta Z = 3$ than for $\Delta Z = 2$. Thus if this were the mechanism causing the spin-density oscillations, it would predict about a factor of 2 smaller hyperfine field for Si ($\Delta Z = 3$) than for Al ($\Delta Z = 2$) (Fe is assumed to have one conduction electron so $Z = 1$). The field of Si in dilute Fe alloys has not been measured. But in the ordered alloy Fe_3Si we observed a field of 37 kG at the Si atom, and in Fe_3Al the field at the Al atom has been measured to about 27 kG.[26] These fields are very close in value and vary in the opposite direction to that predicted by Daniel and Friedel. In Ref. 13(d) we also observed that the first three hyperfine field shifts for the three impurity atoms, Al, Si, and Mn were about the same. This also seems at variance with the results of Ref. 23.

We obtain a rough estimate of the spin-density oscillations expected from the charge perturbation as follows. We first estimate the charge excess (deficit) in a near-neighbor cell to the impurity and then consider different mechanisms for obtaining a spin-density change from this excess charge. We obtain the magnitude of the charge-density perturbation as a function of distance from the impurity from the latest calculation of Singwi *et al.*[27] which includes electron correlation effects and assumes a δ function for the impurity charge distribution. Assuming 1 conduction electron per Fe atom we have $r_s \sim 3$ (see Ref. 27). By integrating Fig. 6 of Ref. 27 we obtain an electron deficit δn in the region of the 1nn distance from a Si impurity atom. Assuming $\Delta Z = +3$ for Si, a generous estimate gives $\delta n \sim 0.04$ electrons. We now consider two possibilities for these deficit electrons: The first assumes that the shielding is done by the $4s$ conduction electrons and the second that the shielding is due to $3d$ electrons. The second case is generally considered to be the more likely since for transition elements the d band has a large density of states. We use both types of estimation just to show that either way the effect is very small. For the first case the change in field, ΔH, will be given by $p\delta n H_{4s}^{Fe}$, where p is the polarization in the region of 1nn distance and H_{4s}^{Fe} is the hyperfine field produced at the Fe nucleus by one $4s$ electron (= 2 MG, see I). We measured this polarization to be about -1.5%. This yields $\Delta H \sim 1.2$ kG at the nearest-neighbor Fe, which corresponds to a percentage shift of about 0.4%. For the second estimate where the shielding is done by the $3d$ electrons we obtain a deficit $3d$ moment of $\Delta m \sim 0.04\ (N_\uparrow - N_\downarrow)/(N_\uparrow + N_\downarrow)$ in the 1nn region, where we assume the electrons near the Fermi level do the shielding and $N_\uparrow, N_\downarrow$ are the density of states of the up and down $3d$ electrons at the Fermi level. An upper limit for the ratio of $N_\uparrow/N_\downarrow$ from the band calculations[28] is about 2. Using the values of H_{cp} and H_s given from the band calculation in Table I we thus obtain a decrease in the 1nn field of $\Delta H \sim (0.04/3)(195/2.2) = 1.2$ kG. This again corresponds to a 0.4% shift. Both these estimates are about a factor 20 smaller than the 8% shift measured for nearest-neighbor Fe atoms to a Si impurity atom. We thus conclude that insofar as these effects can be separated, the observed field shifts are due to the direct spin perturbation, *not* the charge perturbation.

V. ORIGIN OF HYPERFINE FIELDS AT SOLUTE ATOMS IN Fe: VOLUME OVERLAP EFFECT

It has been known for some time that the hyperfine fields at solute atoms in Fe (Co, Ni) show regular variations as a function of atomic number Z.[29] This variation is shown in Fig. 3. The values used were from the compilations in Refs. 30 and 31, and more recent values.[32] It has been realized for some time that the behavior in the regions near the end of the d transition-series elements could be characterized by a field due to these solute atoms having developed a moment. The moments correlate fairly well with those deduced from neutron magnetic scattering experiments,[12] except for Mn (see Ref. 31). However, for the nontransition-series elements no satisfactory interpretation exists. We show here that a simple misfit volume effect easily reproduces all the features observed.

We can consider the solute-atom hyperfine field H_Z as composed of three contributions, i.e.,

$$H_Z = H_C^Z + H_M + H_V \ . \tag{4}$$

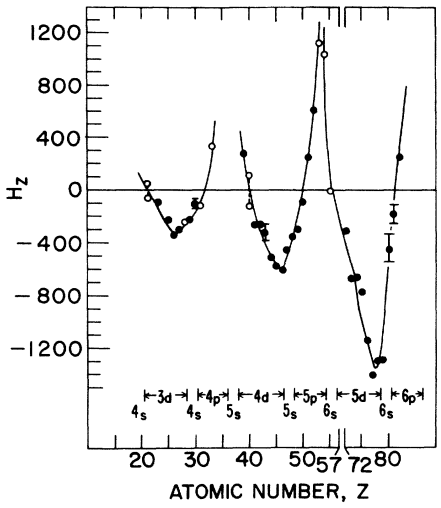

FIG. 3. Solute atom hyperfine field variation (in kG) with atomic number Z; •, sign measured; ○, sign not measured. Where no error flags are shown, the error is within the size of the data points.

The first term is the hyperfine field contribution from the polarization of the conduction electrons by all the Fe neighbors. It can be obtained from

$$H_{\Sigma}^{Z} = (H_{ns}^{Z}/H_{4s}^{Fe})H_{\Sigma}^{Fe} \quad , \tag{5}$$

where H_{ns}^{Z} is the hyperfine field at a nucleus of atom Z due to 1 ns electron. We make the reasonable assumption that the s conduction electrons take on the wave-function character of the s valence electrons of an atom when in the vicinity of its nucleus. Values of H_{ns}^{Z} have been given and discussed by Shirley and Westerbarger[33(a)] and Kopfermann.[33(b)] We use extrapolated values which agree with these works. From Table I H_{Σ}^{Fe} is about − 145 kG. The second term, H_M, is the hyperfine field produced if the solute atom develops a moment. It is composed of two contributions: one from the solute atom core electrons, the other from the self-polarization of the conduction electrons by the solute atom itself. The third term, H_V, becomes important for the nontransition-series elements and is the one we are interested in identifying. Considering only the elements with no moment, we have $H_M = 0$ so

$$H_V = H_Z - H_{\Sigma}^{Z} \tag{6}$$

Now let us assume the following model. Suppose the undissolved solute atom has two outer ns electrons (most of them do, and we will consider the exceptions below) and has a volume V_0 available upon replacement of an Fe atom in an Fe lattice. Suppose further that upon solution an integrated electron density equal to one ns electron goes into the Fe conduction band and the remaining integrated electron density of one ns valence electron (in a virtual bound level connected with the conduction band) is responsible for the hyperfine field contribution, H_V. The polarization of the remaining ns electron is then given by

$$p(Z) = H_V/H_{ns}^{Z} \tag{7}$$

This quantity can be obtained from Eqs. (5) and (6) and is shown in Fig. 4 as the data points with the solid curve through them. The error flags on circles are from uncertainties due to the measured hyperfine fields; those on squares are from uncertainties due to the hyperfine field constants. We find that the remaining ns electron density obtains a positive polarization proportional to the direct overlap of the solute atomic volume V_Z, with the Fe matrix or

$$p(Z) = C(V_Z - V_0) \, . \tag{8}$$

This quantity is shown as the dashed curve in Fig. 4. We use atomic radii values given in Ref. 34 for metals, ionic radii for the halogens, and extrapolated van der Waals's radii for the rare gases. V_0 is evaluated to be 14.6 Å^3. This corresponds to a radius r_0 of 1.5 Å, which is slightly larger than the radius of Fe, 1.40 Å. $1/C$ is evaluated to be 210 Å^3 which corresponds to a radius of 3.8 Å. We see that all the main features for the nonmoment ele-

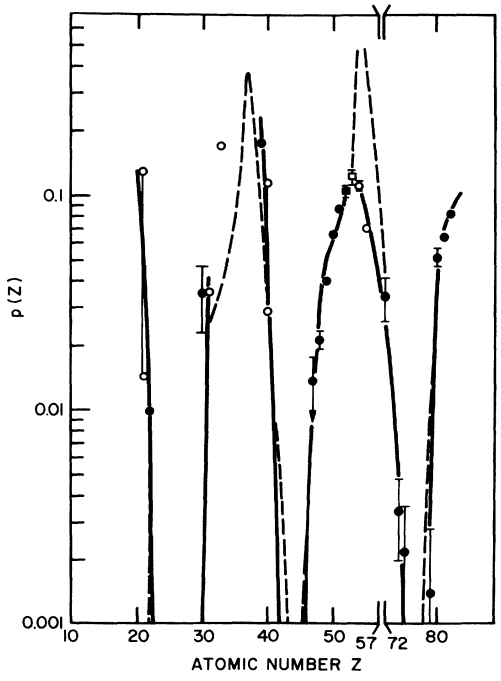

FIG. 4. The solid curve through the data points is $p(Z) = H_V/H_{ns}^{Z}$. The dashed curve shows the positive polarization proportional to the overlap volume $p(Z) = C(V_Z - V_0)$. Where no error flags are shown, the error is within the size of the data points.

ments are successfully reproduced by the overlap volume model. Let us now consider those elements without two outer ns electrons. Cu, Ag, and Au have only one outer electron, but do not concern us, since they have $V_Z \leq V_0$ and thus have little or no H_V term. The rare gases and alkali metals have no and one outer ns electrons, respectively, and do have large radii. Thus they would be expected to deviate considerably from the above model. Of this group only the hyperfine fields of Xe and Cs have been measured and indeed they are, respectively, factors of 7 and 6 lower than would be expected if they had two outer ns electrons. The only other element that differs considerably from the dashed curve is As, which is off by a factor of 5. However, its measured value seems to be way out of line with all the others and may indeed be in error. Its value is only given in Ref. 31 as a result of a private communication. If the 4s conduction band of Fe received less than one electron, the essential results derived here would be the same; but $p(Z)$ would be changed by a scale factor. However, due to the uncertainties in all the quantities involved (i.e., in H_Z, H_C^{Fe}, and H_{ns}^Z) the assumption of one electron per atom in the conduction band seems justifiable and gives reasonable polarization values. Many other oversimplifications have been made, e.g., we have not considered the admixing of the ns, np, and $(n-1)d$ states. Whereas some admixing undoubtedly occurs, the predominant behavior seems to be representable by the polarization of ns-type electrons due to the overlap volume effect since this reproduces all the main features of the H_Z behavior.

This picture agrees well with the usual assignment made of charge difference.[35] $\Delta Z (= Z - 1)$ is usually taken as the charge difference of the impurity with respect to the host (where Z_{Fe} is assumed to be +1). Thus we picture a charge ΔZ shielding the solute atom with the outer ns electrons essentially occupying a volume equal to the atomic volume. This is compatible with calculations of charge screening in Ref. 27, since the solute-atom radius is less than or comparable to the radius of the first node of the charge impurity screening.

We now see that the moments extrapolated from hyperfine fields agreed fairly well with those obtained from neutron experiments, because for greater than the second or third atom in each of the d transition series, V_Z is smaller than V_0, so $H_V = 0$. Using the values of H_C^{Fe} and H_M^{Fe} $(= H_{cp} + H_s)$ obtained in this work (Table I) we can derive more reliable values of H_M^Z than those given previously.[31] These are listed in Table III along with the moment values derived under the assumption that the hyperfine field per Bohr magneton H_M^{nd} has a constant value for each transition series. (This assumption is probably not good to better than 30%; see Ref. 21.) We have used the values given in Ref. 31 for H_M^{4d} $(-370\ \mathrm{kG}/\mu_B)$[36] and H_M^{5d} $(-1180\ \mathrm{kG}/\mu_B)$.[37]

We can also now establish criteria as to which solute atoms are best to use in order to study the Fe matrix itself. We want an atom that develops no moment, does not change the Fe moment, and has no H_V term to interfere with the spin density of the Fe. Looking at atomic radii we see that Al may have a small H_V term whereas Si does not. Thus the Δ_1 value from FeSi alloys $(-0.08\, H_{Fe})$ is probably more indicative of the Fe lattice itself than that from FeAl alloys $(-0.07 H_{Fe})$. That is, it appears that the positive polarization from the Al solute atoms may reduce the polarization of the nearest-neighbor Fe atoms, giving a Δ_1 for FeAl alloys which is slightly too small. Other solute atoms that satisfy the criterial of having a small enough volume are Be, B, C, N, O, P, Cu, Zn, and perhaps Ag. However, all but Be, Zn, and perhaps P have negligible solubility in the bcc phase of Fe. Many other solute atoms in Fe have been observed to give the first-neighbor field shifts Δ_1 which are in the range of $-(0.07$ to $0.08) H_{Fe}$; however, in view of the contributions from H_M^Z and H_V terms that we know can exist, these other solutes cannot be used to obtain reliable Δ_N values for the Fe matrix.

All the above considerations will also apply to solute atoms in Co and Ni.

VI. VARIATION OF FREQUENCIES WITH ALLOYING: VOLUME DEPENDENCE OF THE HYPERFINE FIELD

Many attempts have been made to correlate hyperfine field changes with magnetization changes. The usual assumption made is that $\nu \sim A\sigma$, where A is the hyperfine field constant and σ the saturation magnetization. The variation of the behavior of ν and σ with pressure has thus been attributed to the

TABLE III. Derived values of H_M^Z and the moments of solute atoms in Fe.

Solute	$-H_C^{Fe}$ (kG)	H_M^Z (kG) $(H_V = 0)$	μ (in μ_B) $(H_M^{3d} = -90\ \mathrm{kG}/\mu_B)$
Mn	130	−100	1.1 ± 0.2
Fe	145	−195	2.2
Co	160	−130	1.5 ± 0.1
Ni	175	(−)60	0.7 ± 0.2 (If $H_M^{4d} = -370\ \mathrm{kG}/\mu_B$)
Nb	210	−50	0.1
Mo	240	−16	0.04
Ru	295	−200	0.55
Rh	325	−225	0.6
Pd	360	−230	0.6 (If $H_M^{5d} = -1180\ \mathrm{kG}/\mu_B$)
Re	770	+10	0.0
Os	905	−225	0.2
Ir	1010	−390	0.3
Pt	1160	−120	0.1

pressure dependence of A.[38,39] We show here that the situation is probably much more complex than is usually assumed. In Sec. IV C of I we discussed the saturation or shielding effects of one Fe atom by another in the same alloy. This is manifest in Fig. 3 of I by the *change* in spacing between the lines for a given type site, e.g., the difference in spacing between $D_0 - D_1$ and $D_1 - D_2$ lines, etc., due to different numbers of 2nn's around D atoms (in the same alloy). However, there is also another separate effect noticeable in Fig. 3, namely, the change in frequency with alloying for a given type configuration. This is manifest by the slope in the lines. In the following treatment we assume that these observed frequency variations with alloying are entirely due to the volume change upon alloying. Even if this is not so, the procedure used here is more complete than those used previously.

For an Fe lattice we have $H_{\mathrm{Fe}} = H_{\mathrm{cp}} + H_{\mathrm{ce}}$, where $H_{\mathrm{ce}} = npH_{4s}^{\mathrm{Fe}}$ and p is given by a function somewhat similar to Eq. (3). As we saw in Sec. III there is likely a considerable interband mixing contribution but it is of much the same form[3(d)] as Eq. (3), so we assume

$$H_{\mathrm{ce}} \simeq -\frac{n^2}{E_F} J(0)\sigma \sum_{N=0} w_N f_N F(2k_F R_N) H_{4s}^{\mathrm{Fe}} \quad , \qquad (9)$$

where R_N are the lattice points, f_N is the number of atoms in each neighbor shell, w_N is proportional to the moment and is 1 for D-type and 0.65 for A-type Fe atoms, and $F(2k_F R_N) = [2k_F R_N \cos(2k_F R_N) - \sin(2k_F R_N)]/(2k_F R_N)^4$. We have assumed the entire magnetization is due to electron spin, i.e., no orbital contribution. The usual assumption is that H_{cp} does not change with changes in volume or pressure. To avoid this assumption let us first look at the Si_0^0 solute atom. Here H_V and $H_M = 0$ so we have

$$\nu_{\mathrm{Si}} \simeq H_{\mathrm{Si}} \simeq -\frac{n^2}{E_F} J(0)\sigma H_{3s}^{\mathrm{Si}} \sum_{N=1} w_N f_N F(2k_F R_N) \quad , \qquad (10)$$

and we sum from first neighbors on out. We now assume that the slope in the Si_0^0 line of Fig. 3 of I is due to the change in lattice spacing with alloying. Since the ordered FeSi alloys behave so similarly to Fe we shall further assume that they have proper ties similar to the pure Fe lattice. The change in frequency with volume of the Si atom is then given by

$$\frac{\partial \ln \nu_{\mathrm{Si}}}{\partial \ln V} = -\frac{\partial \ln E_F}{\partial \ln V} + \frac{\partial \ln n}{\partial \ln V} + \frac{\partial \ln \sigma}{\partial \ln V} + \frac{\partial \ln J(0)}{\partial \ln V} + \frac{\partial \ln [n \sum_{N=1} \omega_N f_N F(2k_F R_N)]}{\partial \ln V} + \frac{\partial \ln H_{3s}^{\mathrm{Si}}}{\partial \ln V} \quad . \qquad (11)$$

Only the third and sixth terms have usually been considered but we see here that many more quantities may give contributions. We now consider each of the terms; their values are listed in Table IV.

Heine[40] found the width of the d band in the $3d$ transition series varies as a^{-5}. Thus the first term would have the value $-\partial \ln E_F/\partial \ln V \sim +5/3$. Also, assuming an itinerant electron model with a single parabolic band, Uhrig[41] found that for permalloy films $\partial \ln E_F/\partial P = 8.4 \times 10^{-4}$ kbar^{-1}. As a rough estimate we assume Fe has the same value and using the compressibility of Fe we obtain $-\partial \ln E_F/\partial \ln V \sim +1.4$. We thus list +1.5 for this quantity in Table IV.

Ingalls[42] estimated from Stern's band calculation[43] on Fe that $\partial \ln n/\partial \ln V \sim +0.1$ ($n \sim 1$ electron/atom); this may be quite inaccurate. Anyhow the second term is likely quite small. The third term can be evaluated from the measured values of $(\partial \ln \sigma/\partial P)_T$ and the compressibility: its value is +0.52 for Fe. We crudely estimate the fourth term by considering the forms of $J(\vec{k}, \vec{k}')$. We only consider the Zener term ($\vec{k} = \vec{k}'$). Further, assuming the often-used approximation that there is no overlap of the wave functions we obtain roughly $J(0) \sim nN_d/a$, where a is the lattice parameter and N_d is the number of d electrons per atom, and is proportional to σ. Thus

$$\frac{\partial \ln J(0)}{\partial \ln V} \simeq \frac{\partial \ln n}{\partial \ln V} + \frac{\partial \ln \sigma}{\partial \ln V} - \frac{1}{3} \sim +0.3 \quad .$$

The contribution from the fifth term comes entirely because of the variation in n, since $k_F = (6\pi^2 n)^{1/3}/a$ and R_N is a constant times the lattice parameter, and thus $k_F R_N = \mathrm{const} \times n^{1/3}$. Assuming the given analytical form of $F(2k_F R_N)$ we evaluate this term to be $\sim -3\, \partial \ln n/\partial \ln V$ for $n = 1$ electron/atom.

We would expect the sixth term, the volume dependence of the hyperfine field constant, to be neg-

TABLE IV. Estimation of terms in expression for $\partial \ln \nu/\partial \ln V$.

Term	Quantity measured or estimated	Value
	$(\partial \ln V/\partial P)_T = -5.95 \times 10^{-4}$ kbar^{-1} [a]	
(1) $-\partial \ln E_f/\partial \ln V$		$\sim +1.5$
(2) $\partial \ln n/\partial \ln V$		$\sim +0.1$
(3) $\partial \ln \sigma/\partial \ln V$	$\partial \ln \sigma/\partial P = -3.1 \times 10^{-4}$ kbar^{-1} [b]	+0.52
(4) $\partial \ln J_s(0)/\partial \ln V$		$\sim +0.3$
(5) $\partial \ln(n\Sigma)/\partial \ln V$	$\sim -3\, \partial \ln n/\partial \ln V$ (for Si and D)	~ -0.3
	$\sim -\partial \ln n/\partial \ln V$ (for A)	~ -0.1
	$\partial \ln \nu_{\mathrm{Si}}/\partial \ln V$	$+0.3 \pm 0.2$
$\partial \ln \nu_{\mathrm{Fe}}/\partial \ln V$	$\partial \ln \nu_{\mathrm{Fe}}/\partial P = -1.6 \times 10^{-4}$ kbar^{-1} [c]	+0.27
	$\partial \ln \nu_A/\partial \ln V$	$+1.2 \pm 0.4$
	$\partial \ln \nu_D/\partial \ln V$	-0.8 ± 0.2

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[c] Reference 38.

ative for a Si atom. A decrease in volume should increase the number of conduction electrons at the Si nucleus. Since the conduction electrons at the Si nucleus are predominantly negatively polarized by the first and second nearest neighbors, and since the hyperfine field is negative (because of this negative polarization from 1nn and 2nn shells), we would thus expect the hyperfine field to become more negative (or $\partial \ln H_{3s}^{Si}$ to increase) with a decrease in volume. This does *not* imply that the conduction electrons are negatively polarized as Anderson[39] has argued [we find + (5–8)%], but occurs because the 1nn and 2nn happen to be at a distance such that they give a negative contribution to the hyperfine field.

We evaluate $\partial \ln\nu_{Si}/\partial \ln V$ from the slope of the Si_0^0 line and the known lattice parameter variation[44] with alloying. The data points shown in Fig. 3 in I have not been corrected for the shift due to the 9nn broadening. Making this correction assuming the 9nn shift is negative and all the broadening is due to the 9nn (as can be seen from Fig. 1 the 9nn appears to be near a minimum of an oscillation so we would expect that the broadening of Si_0^0 is nearly all due to this shell), we obtain $\partial \ln\nu_{Si}/\partial \ln V \sim +0.3 \pm 0.2$ as a reasonable estimate. Using the values listed in column 3 of Table IV we thus find $\partial \ln H_{3s}^{Si}/\partial \ln V \sim -1.8$, which is negative as expected. We emphasize, however, that many of the values listed in Table IV are only tentative estimates.

Let us now consider the Fe atoms. For them we have $H_{Fe} = H_{cp} + H_{ce}$, where now we include the point at the origin in H_{ce}, i.e., the self-polarization term. Thus we obtain

$$\frac{\partial \ln\nu_{Fe}^{A,D}}{\partial \ln V} = \frac{H_{cp}\,\partial \ln\nu_{core}^{A,D}}{H_{Fe}\,\partial \ln V} + \frac{H_{ce}}{H_{Fe}}\left(\frac{\partial \ln np_{Fe}}{\partial \ln V} + \frac{\partial \ln H_{4s}^{Fe}}{\partial \ln V}\right), \tag{12}$$

where $\partial \ln np_{Fe}/\partial \ln V$ is similar to the first five terms in Eq. (11) (the fifth term has $\sum_{n=0}$ instead of $\sum_{n=1}$). From Table I, $H_{cp}/H_{Fe} \simeq 1.2$ and $H_{ce}/H_{Fe} \simeq -0.2$. Usually $\partial \ln\nu_{core}/\partial \ln V$ has been assumed to be zero, but we see from the slopes of the A and D lines in Fig. 3 in I that for these alloys this does not appear to be so. In order to evaluate the $A_{4,5}^{12}$ frequency change with volume the $A_{4,5}^{12}$ values must be corrected for the broadening of the 7nn and 10nn shells. Assuming that the shift due to the 10nn shell is negative and about $\frac{1}{2}$ that of the positive 7nn field shift we get $\partial \ln\nu_A/\partial \ln V = +1.2 \pm 0.4$. For D_0 atoms we get $\partial \ln\nu_D/\partial \ln V = -0.8 \pm 0.2$. Aside from the core term and the $\partial \ln n\sum/\partial \ln V$ term, all other terms in Eq. (12) should be the same for A and D Fe atoms. We estimate the values of the latter and find the values listed in Table IV. Although these are different for the two types of Fe atoms (due to the very different environments of A and D) they are both small and it seems unlikely that the different slopes of the A and D atoms can be attributed to this term. This leaves the core term as the most likely source for the difference in slopes. It is known from polarized neutron experiments[45] on Fe_3Al that the A and D Fe atoms have different orbital distributions. Both types of atoms have more e_g magnetic electrons than corresponds to spherically symmetry (40% e_g–60% t_{2g}); the A type were measured to have 48% e_g– 52% t_{2g} and the D type 60% e_g–40% t_{2g}, whereas pure Fe has 53% e_g–47% t_{2g}. Thus both A- and D-type atoms deviate from spherical symmetry with an excess of magnetic electrons along the bcc edge directions. It was essentially assumed in the above neutron experiment that the radial distributions of A- and D-type atoms were the same. The slope for the D atoms indicated that upon decreasing the volume the relative number of spin-down electrons at the nucleus increases, whereas the slope for the A atoms indicates that the density of spin-up electrons increases. The different angular (and possibly radial) distributions for the A and D atoms make it possible that there may be different behavior of the core hyperfine fields for the two types of atoms. Since the frequency change with volume of Fe is so close to that of Si, it may be that $\partial \ln H_{cp}/\partial \ln V$ is near zero for Fe.

If there is a change in the core contribution to the hyperfine field of the type discussed above it should not affect the measurements and interpretation of the hyperfine field shifts as due to CEP. For a given alloy each type Fe atom (D or A) will have essentially its own core distortion (as evidenced by the fact that the lines in Fig. 3 in I are parallel for each type Fe atom), but we measure relative shifts with respect to this distortion.

VII. CONCLUSIONS

By summing the CEP contributions from all the neighbors in a pure Fe lattice we find the hyperfine field contribution from the Fe neighbors. Using the latest Fe band calculation for the core contribution we can obtain the self-polarization contribution to the hyperfine field. This gives the CEP at the origin. The resulting CEP distribution agrees reasonably well with the improved RKKY-type spin-density calculations including interband mixing and we find $J(q=0) \sim 0.5$ eV. This is similar to the values of $J_{eff}(0)$ obtained from experiments on dilute alloys of Mn in nontransition metals. We find a net *positive* CEP of about + (5–8)% for the 4s-like electrons. The CEP is seen to be directly due to the magnetic moment perturbation, the effect of the charge perturbation being much smaller.

Using the value obtained for the hyperfine field due to the neighboring Fe atoms we can success-

fully interpret the variation of hyperfine field observed at solute atoms in an Fe lattice. We find that there is a positive polarization term proportion to the volume overlap of the solute atom with the Fe matrix.

Finally we show that the variation of the hyperfine field with changes in pressure or volume depends on many more quantities than the hyperfine field constant and saturation magnetization as is usually assumed.

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Thermoelectric Power of a Two-Band Ferromagnet*

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Recently it has been proposed that "magnon drag" is responsible for the very large peak in the thermopower of iron near 200 K. We report here the results of calculations which, while they do not discount the possibility of magnon-drag contributions, do indicate that the peak could be accounted for empirically by the transport process occurring in two overlapping bands under the influence of a very large internal magnetic field. It is speculated that the spin-orbit interaction may be the real source of the large peak in the thermoelectric power.

Recently it has been proposed that "magnon drag" is responsible for the very large peak in the thermoelectric power of iron near 200 K. We report here the results of calculations which, while they do not discount the possibility of magnon-drag contributions, do indicate that the peak could be accounted for empirically by the transport process occurring in two overlapping bands under the influence of a very large internal magnetic field simulating the effect of the spin-orbit interaction on the thermoelectric power.

Bailyn[1] suggested that the absolute thermoelectric power or the Seebeck coefficient S of ferromagnetic metals may exhibit a magnon-drag effect similar to the phonon-drag effect[2] found in pure elements and in dilute alloys. These drag effects are assumed to be responsible for large deviations from the expected linear temperature dependence of S due to the "diffusion" term,[3]

$$S_{\text{diff}} = -\left(\frac{\pi^2 k^2 T}{3|e|}\right)\left(\frac{\partial \ln\sigma(E)}{\partial E}\right)_{\text{Fermi level}}, \tag{1}$$

with the temperature dependence of the term in the second large parentheses assumed to be small.

The general temperature dependence of the phonon drag and the proposed magnon-drag contributions are rather similar.[1] However, Blatt *et al.*[4] argued that the very large peak in S of iron is due to a magnon-drag and not a phonon-drag term, since it is found also in dilute alloys and is not removed by cold work, as phonon-drag contributions are. The first argument may be questionable. If phonon-drag and magnon-drag effects are similar, one would expect that impurities would affect these contributions similarly. Furthermore, Farrell and Grieg[5] have shown that changes in the phonon-drag contributions due to alloying can be accounted for using the concept of "spin mixing" and a two-band description of the transport process. Thus it seems reasonable that the peak in S of iron may be partly due to the transport process occurring in several energy bands.

The nature of transport processes in ferromagnets with their so-called "spontaneous" components in a magnetic field has led us to propose that the diffusion thermoelectric power is also augmented by the presence of anisotropic electron scattering resulting from the spin-orbit interaction.

The spin-orbit interaction is generally believed to account for the large electric Hall field E_H that occurs when the applied field H is strong enough to align all the magnetic domains parallel with one another. The observed Hall field is very much larger than that necessary to oppose the sideways deflection of the electrons due to the Lorentz force. The additional Hall field strength is needed to oppose the transverse current arising from the anisotropic electron scattering induced by the spin-orbit interaction. This anisotropic scattering may be simulated by a magnetic field, H_{so}, which acts on the electrons like an applied field. The "effective" magnetic field, $H_{\text{eff}} = H_{\text{applied}} + H_{so} \gg H_{\text{applied}}$, thereby gives a much larger Lorentz force and Hall field, $\vec{E}_H = R\vec{H}_{\text{eff}} \times \vec{j}$, where R is the Hall coefficient and $\vec{j}$ is the external current, as is observed in ferromagnets.

The effect of the spin-orbit interaction in the diffusion thermoelectric power may also be simulated by a large effective magnetic field interacting with the diffusing electrons via the Lorentz force. This empirical simulation seems justified as the more rigorous calculation of the "skew" scattering con-