Systematics of Hyperfine Fields in an Iron Lattice*

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A survey is presented of the observed hyperfine fields at nuclei of impurities dissolved in metallic iron. Estimates are made from atomic hfs constants of the contributions to internal fields that might be expected on the basis of conduction-electron polarization. The observed fields in several heavy elements are roughly proportional to the fields attributed to the outer s electrons in the free atoms. The signs and magnitudes, and especially the Z dependence, of these fields are compatible with the conduction-electron polarization mechanism. Other internal fields, particularly for Cs and Ba in Fe, are predicted, to test this mechanism further. A tentative basis is thus established for estimating the hyperfine fields at impurities in iron. These estimates should be useful in planning Mössbauer or nuclear polarization experiments.

I. INTRODUCTION

DURING the course of the work on silver reported in the preceding paper we surveyed the available data on hyperfine fields in magnetic metals. Certain systematic trends emerged that are consistent with interpretation on a very simple picture. This is especially true of that part of the internal field that we attribute to conduction-electron polarization (CEP), in which the outer s electron of a metallic impurity in, for example, an iron lattice is polarized by exchange[1] and creates a hyperfine field at the impurity nucleus via the Fermi contact interaction.[2]

It is not feasible to calculate internal hyperfine fields from first principles. The calculations to date have been based on models involving rather substantial approximations. The detailed calculations have been based on *atomic* properties, rather than referring in any quantitative way to specifically solid-state properties. In spite of these difficulties the theory has followed experiment rather closely, and several mechanisms have been suggested that are in large part borne out by experiment. We do not propose any new mechanisms here (although we do give a specific recipe for estimating the contributions from CEP), but simply discuss known internal fields in terms of existing mechanisms.

It should be emphasized that the interpretation of induced fields in terms of CEP is not unique. It is very difficult to establish the relative contributions of CEP and core-polarization (CP) experimentally, although we cite some evidence favoring CEP in the heaviest elements in a later section. Surely there is *some* core polarization in any atom on which the outer electrons are not paired exactly to zero. This survey should be useful primarily in helping to categorize the known hyperfine fields for solutes in iron. These fields have considerable practical importance (particularly for nuclear orientation) and a qualitative understanding of their origins, or at least a systematic method of predicting them, is badly needed. A secondary purpose of this paper is to suggest that the rather sparse data available at present seem to favor CEP as a field-producing mechanism for silver and some of the heavier elements in magnetic hosts.

A tabulation of measured hyperfine fields at nuclei in Fe, Co, and Ni lattices is given in Sec. II, and evidence for an inductive mechanism for some of these fields is discussed in Sec. III. Several mechanisms are reviewed in Sec. IV. In Sec. V a method is given for estimating contributions from CEP. This is compared with experiment in Sec. VI, and Sec. VII contains several predictions that arise from this comparison.

II. THE MEASURED HYPERFINE FIELDS

We are concerned here with hyperfine magnetic fields at nuclei of impurity atoms dissolved (presumably in very dilute, substitutional, primary solid solutions) in ferromagnetic metals. Only the hosts Fe, Co, and Ni are considered because only for these hosts are enough data available to allow a disscusion of systematic behavior. The fields are set out in Table I with errors, where available, in parentheses. Signs are given for the cases in which they are available.

III. EVIDENCE FOR INDUCTION

In the $3d$ transition group ferromagnetism is thought to arise from unpaired spins of the $3d$ electrons. The hyperfine fields are also attributable to these spins, albeit for the most part indirectly. From a strictly empirical point of view, evidence that the internal fields at nuclei of normally diamagnetic atoms dissolved in magnetic lattices are induced by the unpaired $3d$ spins of host atoms may be derived from the approximately proportional behavior exhibited in Fig. 1, where these fields are plotted against the effective moments of the hosts, after Roberts and Thomson,[3] who made such a plot for gold. For Au and Ag, with nominally filled

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[1] R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961). In this excellent discussion of the origins of effective fields, several mechanisms that give rise to hyperfine fields are described. We refer to this discussion throughout this paper.

[2] E. Fermi, Z. Physik **60**, 320 (1930).

[3] L. D. Roberts and J. O. Thomson, Phys. Rev. **129**, 664 (1963).

TABLE I. Hyperfine fields in Fe, Co, and Ni hosts.

Atom \ Host	Fe	Co	Ni	Ref.[a]
Sc	100(30)			b
V	87.3(3)			c
	90(30)	183	≤60	d
Cr	<100			e
Mn	270(15)	200(15)	−316(10)	d
	225.5(5)		325	c, f
Fe	−339	−329	283	g, h
Co	−286.3	−215.0	−120	g, h, i, j
Ni	235	189	74.8	g
Cu	−212.7	157.5	−47.2	g, k
Y	+205			k
Zr	125			l
(in $ZrFe_2$)				
Ru	505(20)		−178(7)	m
Ag	−272(19)		−84(5)	n
Cd	348(10)		65.3(1.6)	o
In	250			p
Sn	−81(4)	−20.5(1.5)	+18.5(1.0)	q
Sb	193(3)			r
	+205			k, s
	170(8)			t
Te	+620(20)		+195(10)	u
Ta	−250			v
W	760(80)			w
Re	−560			v
	610(35)			t
Os	1430			x
Ir	−1350(300)			y, z
	−840			aa
	−1240(220)			bb
Pt	−1080			aa
	1390			x
	1600(300)			cc
Au	−1420(180)	−980(180)	−340(60)	dd
	1460(160)	1180(120)	420(120)	ee
	1350(50)			ff
	−1000		−180	gg
Hg	−980(280)			hh

[a] Signs of hyperfine fields are given where known. Error limits are stated parenthetically for some cases. For cases in which fields are known at several temperatures the lowest-temperature values are given. For some cases in which two or more values are given there is apparent disagreement, but this may not be real because samples of different compositions may have been used. Original references should be consulted.

[b] V. Kogan, V. D. Kul'kov, L. P. Nikitin, N. M. Reinov, I. A. Sokolov, and M. F. Stel'makh, Zh. Eksperim. i Teor. Fiz. **39**, 47 (1960) [English transl.: Soviet Phys.—JETP **12**, 34 (1961)].

[c] Y. Koi, A. Tsujimura, and T. Hihara, J. Phys. Soc. Japan **19**, 1493 (1964).

[d] J. A. Cameron, I. A. Campbell, J. P. Compton, M. F. Grant, R. W. Hill, and R. A. G. Lines, paper CM 14 given at the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio, September 1964 (unpublished).

[e] B. N. Samoilov, V. V. Sklyarevskii, and E. P. Stepanov, Zh. Eksperim. i Teor. Fiz. **36**, 1944 (1959) [English transl.: Soviet Phys.—JETP **9**, 1383 (1960)]. These authors reported a γ-ray anisotropy of <0.5% for Cr^{51} in Fe, from which we have calculated this limit for the field.

[f] Y. Koi and A. Tsujimura, J. Phys. Soc. Japan **18**, 1347 (1964).

[g] A. M. Portis and R. H. Lindquist, in *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2, Chap. 4. This review article contains references to nuclear resonance work on ferromagnetic materials.

[h] A. J. Freeman and R. E. Watson, in *Magnetism: A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. 2. This review article contains references to many papers on hyperfine fields.

[i] G. A. Westenbarger and D. A. Shirley, preceding paper. Phys. Rev. **137**, A161 (1965).

[j] The sign of the field for Co in Co is inferred from the sign for Co in Fe and the continuous variation of the field for Co in Co-Fe alloys. We thank A. M. Portis for pointing out this argument.

[k] B. N. Samoilov, postdeadline paper given at the Ninth International Conference on Low-Temperature Physics (unpublished), and private communication to G. A. Westenbarger.

[l] H. Betsuyaku, S. Komura, and Y. Betsuyaku, J. Phys. Soc. Japan **19**, 1262 (1964).

[m] The first value, 500 kG, for Ru in Fe was given by O. C. Kistner and R. Segnan, Bull. Am. Phys. Soc. **9**, 396 (1964). The present value (which is preliminary) was obtained by comparison of Kistner's data [O. C. Kistner (private communication)] with data on the excited-state moment in Ru^{99} (E. Matthias, S. S. Rosenblum, and D. A. Shirley, to be published). The Ru-in-Ni field is reported in this latter reference.

[n] See *Note added in proof*, of Ref. i.

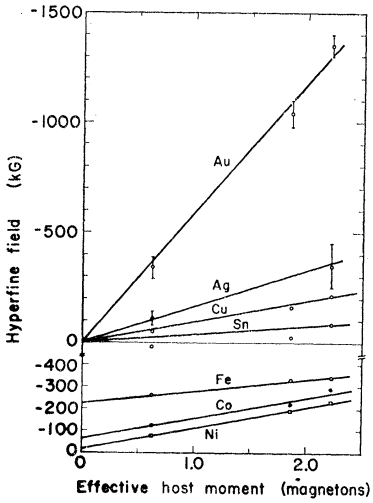

FIG. 1. Hyperfine fields at nuclei of atoms dissolved in Fe, Co, and Ni lattices, plotted against the host magnetic moments. The signs of the fields are known in most but not all, cases (see Table I). Where unknown, they have been plotted as negative. The upper four atoms are nominally diamagnetic. Except for Sn, the hyperfine fields in these atoms are roughly proportional to the host moments, suggesting an inductive mechanism due to the host $3d$ electrons. The lower three atoms are nominally magnetic, and their hyperfine fields show some tendency to be constant.

$4d$ and $5d$ shells, this proportional behavior is to be expected, but it does not allow one to distinguish between the contributions from CEP and CP. For Cu induction is also indicated, but here there may also be unpaired d-electron spins on the Cu atoms leading to CP. For Ir in these three hosts the internal fields have been found to be approximately proportional to the host moments, and of about the same magnitude as the

[o] E. Matthias, S. S. Rosenblum, and D. A. Shirley, Phys. Rev. Letters **14**, 46 (1965), and unpublished data.

[p] B. N. Samoilov, V. V. Sklyarevskii, and E. P. Stepanov, Zh. Eksperim. i Teor. Fiz. **38**, 359 (1960) [English transl.: Soviet Phys.—JETP **11**, 261 (1960)].

[q] A. J. F. Boyle, D. St. P. Bunbury, and C. Edwards, Phys. Rev. Letters **5**, 553 (1960).

[r] E. Sloan, thesis, Harvard University [unpublished data quoted by F. M. Pipkin, J. Sanderson, and W. Wehymann, Phys. Rev. **129**, 2626 (1963)].

[s] A positive sign for Sb in Fe has also been found by A. Stolovy (private communication).

[t] O. V. Lounasmaa, C. H. Cheng and P. A. Beck, Phys. Rev. **128**, 2153 (1962).

[u] R. B. Frankel, J. Huntzicker, E. Matthias, S. S. Rosenblum, D. A. Shirley, and N. J. Stone (to be published).

[v] A. Stolovy (private communication).

[w] E. Kankeleit, Bull. Am. Phys. Soc. **10**, 65 (1965). This value is based on a g factor of +0.22 for the first excited state of W^{182}.

[x] Private communication from J. M. Ho and N. E. Phillips (to be published).

[y] A. V. Kogan, V. D. Kul'kov, L. P. Nikitin, N. M. Reinov and M. F. Stel'makh, Zh. Eksperim. i Teor. Fiz. **45**, 1 (1963) [English transl.: Soviet Phys.—JETP **18**, 1 (1963)].

[z] See Ref. 14 in text.

[aa] A. Stolovy, Bull. Am. Phys. Soc. **10**, 17 (1965).

[bb] J. Huntzicker, E. Matthias, S. S. Rosenblum, and D. A. Shirley (to be published).

[cc] A. B. Buryn and L. Grodzins, Bull. Am. Phys. Soc. **9**, 410 (1964). This is a preliminary result. We have calculated this field from the splitting given by these authors: they indicate that the field is about 10^6 G.

[dd] Reference 13.

[ee] L. D. Roberts and J. O. Thomson, Phys. Rev. **129**, 664 (1963).

[ff] I. A. Campbell, N. J. Stone and B. G. Turrell, Proc. Roy. Soc. (to be published).

[gg] B. N. Samoilov, V. V. Sklyarevskii, and V. D. Godobchenko, Zh. Eksperim. i Teor. Fiz. **41**, 1783 (1962) [English transl.: Soviet Phys.—JETP **14**, 1267 (1962)]. The magnitudes represent lower limits.

[hh] This field may be estimated by combining the g factor of +0.55 for the 412-keV state in Hg^{198} (reported by Körner at the Paris Conference on Nuclear Structure, July, 1964) with the Larmor frequency for this state in an iron lattice reported by L. Kezthelzi *et al.*, Phys. Letters **8**, 195 (1964).

fields for gold.[4] The Ir fields are not yet accurately enough known to be put in Fig. 1. For Ni the field varies almost proportionally with host moment; in this case, however, there are surely unpaired d-electron spins on Ni. Thus the validity of this proportionality in establishing induction is questionable. Of course Ni is "less" magnetic than the hosts Fe and Co, and its larger hyperfine fields in these lattices do presumably arise from induction. In Sn, again, the lack of proportionality suggests that the origins of the internal fields are more complex. This conculsion is supported by the small magnitudes of these fields; this case is discussed in Sec. VI.

For iron itself the hyperfine field is in large part independent of the host's magnetic moment. One would expect an essentially constant (with changing host) hyperfine field for each magnetic $4f$- and $5f$-group element as an impurity because of the large, unquenched orbital contributions, so long as crystal field effects are negligible.

IV. MECHANISMS FOR HYPERFINE FIELDS

The various mechanisms that contribute to hyperfine fields in magnetic metals have been enumerated in several places[5,6] and we review only the most important, in terms of the size of field produced, very briefly here.

The external, Lorentz, and demagnetizing fields are relatively small and known: we assume that they can be accounted for. Direct contributions from the $3d$ electrons are also small, though not necessarily negligible, in most cases. The orbital angular momentum is "quenched" and the dipolar (spin) contribution vanishes for cubic symmetry.[5] The major contributors to hyperfine fields in most cases are CP and CEP.[7] In both of these the d electrons spin-polarize the (core or conduction) s electrons, which create large hyperfine fields via contact interaction at the nucleus. Core polarization is generally regarded as the largest single contributor to the internal field in iron and the other $3d$ magnetic elements.[1]

Spin-exchange polarization of the $4s$ conduction electron of the magnetic atom results in a positive contribution to the hyperfine field at the nucleus of the magnetic atom, but a negative spin density outside the atom. (According to the usual sign convention, internal fields are positive if parallel to the external magnetizing field. Spin polarization is positive if parallel to the $3d$ spins, which are antiparallel to the external field.) This negative spin density can exchange-polarize the s conduction electrons on a neighboring (nonmagnetic) impurity atom and create a large negative field at the nucleus of that atom.[1,8]

V. AN ESTIMATE OF THE CONDUCTION ELECTRON CONTRIBUTION

The mechanism suggested above implies a conduction-electron contribution to the hyperfine field that is proportional to the polarization of conduction electrons at the impurity p, to the hyperfine field created via contact interaction by one electron $H(0)$, and to the number of such electrons n:

$$H_{\mathrm{CEP}}=npH(0). \qquad (1)$$

For most metals n is approximately 1. The exact value of n that is appropriate for any given case could be reliably estimated only by detailed calculations based on the band structure of that particular host-impurity system. At present such calculations are not feasible. Watson and Freeman[1] have calculated the spin density of the $4s$ electron on iron, finding that the $4s$ spins are polarized to the extent of a few percent in the outermost regions of the atom, and that this polarization is *negative* with respect to the $3d$ spins. The exact extent of polarization of the $4s$ electrons in iron metal is somewhat uncertain. It also changes with distance, and we are interested in the polarization induced in the outer s electrons of the impurities [p in Eq. (1)]. This polarization p could only be rigorously calculated from the exchange integral involving the $4s$ electron of Fe and the outer s electron of the impurity.

Until computational methods are developed which make good theoretical estimates of n and p in Eq. (1) possible, the best that we can do is to estimate them. We know from the above discussion that the product np should be a few percent, and *positive* if we are interested in the direction of the hyperfine field, as in Eq. (1) (this results in a *negative* H_{CEP}; it follows from

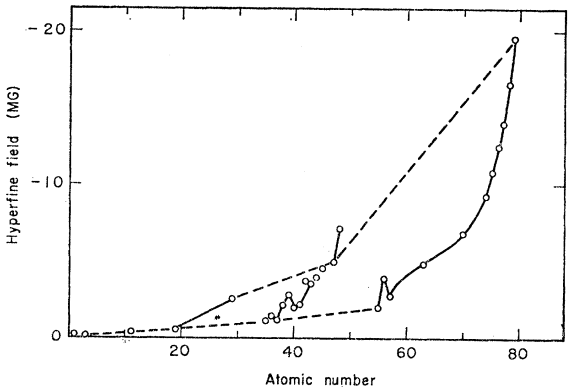

FIG. 2. Hyperfine fields, due to outer s electrons, in free atoms. The alkalis are connected by a dashed curve, as are the Group IB metals Cu, Ag, and Au. Solid curves are drawn through the $5s$ electron series and the $6s$ electron series. These fields were calculated from atomic hyperfine structure constants. A tabulation of references is given by G. Laukian in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 38, Part 1, p. 338.

[4] W. Easley, J. Huntzicker, E. Matthias, S. S. Rosenblum, and D. A. Shirley, Bull. Am. Phys. Soc. **9**, 435 (1964).

[5] W. Marshall, Phys. Rev. **110**, 128 (1958).

[6] A. J. Freeman and R. E. Watson, in *The Mössbauer Effect*, edited by D. M. J. Compton and A. Schoen (John Wiley & Sons, Inc., New York, 1962), p. 117.

[7] The rare earths (and presumably the $5f$ series) are important exceptions. Here in most cases the internal fields arise from the $4f$ electrons. See Sec. VII.

[8] A discussion of this effect is given by E. Daniel and J. Friedel, J. Phys. Chem. Solids **24**, 1601 (1963).

TABLE II. Hyperfine fields arising from outer s electrons of free atoms.

Element	Electron	$-H(0)$ (MG)	Element	Electron	$-H(0)$ (MG)
H	1s	0.166	Ag	5s	4.98
Li	2s	0.121	Cd	5s	7.14
Na	3s	0.394	In	5s	9.14
K	4s	0.580	I	6s	1.71
Cu	4s	2.60	Xe	6s	2.12
Br	5s	1.12	Cs	6s	2.06
Kr	5s	1.45	Ba	6s	3.91
Rb	5s	1.23	La	6s	2.81
Sr	5s	2.11	Eu	6s	4.80
Y	5s	2.82	Yb	6s	6.85
Zr	5s	2.00	W	6s	9.33
Nb	5s	2.23	Re	6s	10.8
Mo	5s	3.70	Os	6s	12.5
Tc	5s	3.48	Ir	6s	13.9
Ru	5s	4.09	Pt	6s	16.6
Rh	5s	4.54	Au	6s	19.6
			Hg	6s	24.2

spin-polarization of the impurity's s electron by the 4s electrons of Fe). It is reasonable to expect that in first approximation the np product will be nearly constant for most heavy metal atoms in iron. We shall find in Sec. VI that the available data are best fitted by $np \cong 0.07$.

Finally, the field at the impurity-atom nucleus arising from one ns electron (here n is the principle quantum number) can be estimated from the atomic hyperfine structure constant a_{ns}, together with the nuclear moment of a given isotope, or simply by using the Fermi-Segrè formula with appropriate modifications. These procedures are thoroughly discussed by Kopfermann.[9] They are too involved to describe in detail here, and Kopfermann's excellent discussion should be referred to for details. It should be noted, however, that the hyperfine field arising from an s electron is not simply $-(8\pi/3)\beta\Psi^2(0)$, but that there is a relativity factor of up to 2 for heavy atoms, in addition to several smaller corrections. There has been considerable criticism of the accuracy of the Fermi-Segrè formula for estimating internal fields. While there is no *a priori* reason to believe that this formula, which was originally applied to alkali atoms, is particularly accurate, in fact its agreement with experiment is, on the whole, quite good. This point has been discussed by Breit.[10] Even if the hyperfine fields in free atoms that are attributed to the ns electrons do arise in part from core polarization, this effect should also be present in metals, and we are only comparing internal fields in metals with those in atoms. Using atomic spectroscopy data, we have calculated the hyperfine fields, arising from contact interaction, for the outer s electrons of several elements. The results[11] are plotted in Fig. 2. Several values are listed in Table II.

The smooth variation of $H(0)$ with atomic number in Fig. 2 is striking. Of particular interest is the variation between the alkalis, which are connected by a curve, and the Group IB metals, also connected with a curve. The series of atoms having outer 5s (6s) electrons are also connected with curves. In going across the 5s series from Rb to Ag the internal field due to the 5s electron increases in magnitude from 1.23 to 4.98 MG. In the 6s series the change is even more pronounced, from 2.06 MG in Cs to 20 MG in Au. These trends are easily understood physically in terms of incomplete shielding of the 4d(5d) shell, as well as relativistic effects. There is a relatively flat portion in the 6s electron curve in the rare-earth region. This presumably arises from the more complete shielding of the 6s electrons from the nucleus by the 4f electrons.

To compare the induced fields for impurities dissolved in iron with the above free-atom fields we adjusted the scale by fitting the internal field for Au in iron. This is equivalent to taking $np=0.07$ in Eq. (1), which has the effect of multiplying the ordinates of the curves in Fig. 2 by 0.07. The resulting plots are compared with experiment in Fig. 3.

Before discussing the comparison with experiment in detail it is well to consider whether $np=0.07$ is reasonable. On the average n is about 1; thus a polari-

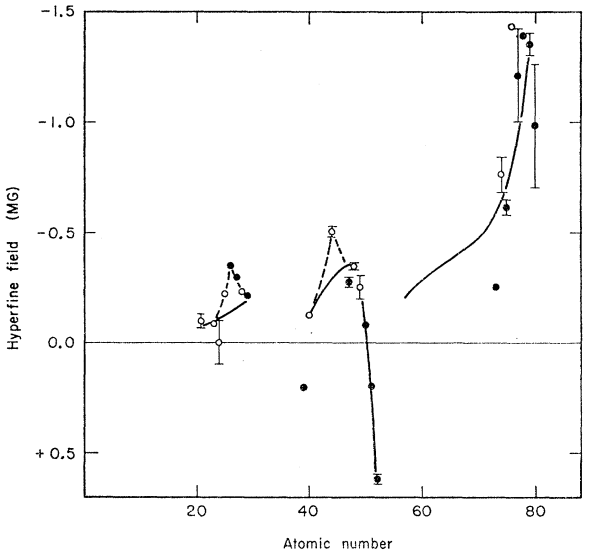

FIG. 3. Hyperfine fields at nuclei of atoms dissolved in an iron lattice. Cases for which the sign is known are shown as filled circles. Curves from Fig. 2, multiplied by 0.07, are superimposed, as solid curves, for the 3d, 4d, and 5d series. We regard these curves as reasonable estimates of the hyperfine fields arising from conduction-electron polarization in the more metallic elements. Dashed lines emphasize the well-defined Slater-Pauling type curve in the 3d series and a possible curve in the 4d series. There is only weak evidence for such behavior in the 5d series, where CP is *relatively* less important than CEP. "Conduction" electron polarization is not relevant to the 5p shell elements, but these points are included for completeness, and a solid curve is drawn through them to emphasize their regularity.

[9] Hans Kopfermann, *Nuclear Moments* (Academic Press, Inc., New York, 1958).

[10] G. Breit, Rev. Mod. Phys. **30**, 507 (1958).

[11] References to optical hyperfine structure data are conveniently found in nuclear moment tabulations. A particularly thorough tabulation, covering the literature up to about 1957, is given by G. Laukian in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 38/1, p. 338.

zation of about 7% is implied. This is a little higher than might be expected from Watson and Freeman's free atom calculations[1] on Fe, although the comparison is not simple. Two factors that have not been taken into account in our estimates of np are (1) the difference between the probability of being at the nucleus of the outer s electron in the free atom and in the metal, and (2) the fact that electron transfer (or a change in electron density) takes place in alloys.[12] For electronegative metals in Fe these two effects will tend to cancel to some extent. For electropositive metals they may tend to decrease the internal fields. It would be very valuable to get independent experimental or theoretical evidence about np for even one case, to test the proposed figure of 0.07.

VI. THE COMPARISON WITH EXPERIMENT

In evaluating Fig. 3 we must remember that observed hyperfine fields for impurities dissolved in iron are being compared with the "expected" contributions from polarized conduction electrons alone. The points corresponding to internal fields caused by core polarization, orbital contributions, etc., should not lie on the "conduction-electron polarization" curves, which should, rather, serve as a baseline from which the fields in magnetic atoms would deviate. We have included magnetic impurity atoms in Fig. 3 for completeness.

It is for the heavier elements that conduction-electron polarization is expected to be a dominant contributor to the induced fields. The qualitative agreement of the 6s electron series with CEP estimates is impressive. The fields are negative in those cases for which the sign is known, the magnitudes are very large, and there is an increase in magnitude by a factor of 2.3 from Re to Au. This last point is explained quite naturally by CEP, while there is apparently no reason to expect such a change in fields arising from CP. Accurate measurements of the internal fields at nuclei of other 5d metals dissolved in iron would be very useful.

The induced fields in In, Sn, and Sb probably have complex origins, and no single mechanism should be expected to account for them. These three elements have filled 5s shells and are quite electronegative, so they probably do not lose electrons in an iron lattice. It seems unlikely that 5s electrons can contribute as fully to the internal fields as is the case in Ag, for example, where there is only one 5s electron beyond the 4d shell (we note that a 5s electron on an atom of In, Sn, or Sb creates a much larger hyperfine field than does a 5s electron on Ag). It is, then, consistent with the CEP systematics that the fields on these atoms are not large and negative.

Figure 3 was first drawn before the hyperfine field for Ag in Fe was available, and it was used to predict[13] an internal field of -400 kG,[11] in fair agreement with the experimental result of -272 ± 19 kG. Silver should be a particularly simple case if the 4d shell is closed, with one 5s electron. The internal field for Ru in Fe is larger in magnitude than that of Ag in Fe: This may suggest core polarization in Ru, and possibly in other 4d-transition-series atoms in an iron lattice.

It is instructive to examine the iron-group points on Fig. 3. For the lighter elements the hyperfine fields are of the order of 100 kG or less, not too far from the CEP curve (here there are several mechanisms that could be as important as CEP, and one cannot infer anything from this approximate agreement. The CEP curve is not expected to be applicable here). The fields rise and fall dramatically for $25\leq Z\leq 29$, in a manner very reminiscent of the Slater-Pauling curve. This is, of course, no surprise, because both the effective magnetic moment, which is the ordinate in the Slater-Pauling curve, and the internal field are caused by unpaired spins in the 3d shell. As impurities in iron these atoms to some extent bring in unpaired spins: to some extent their spins are further unpaired by the ferromagnetic host.

VII. CONCLUSIONS

In this paper we have presented a brief survey of hyperfine fields at nuclei of impurities dissolved in iron. Trends were observed which may prove of some heuristic value. It is very important, for several experimental methods that depend on hyperfine fields in ferromagnets, to be able to make reasonable estimates—however empirical—of the fields that can be expected. Figure 3 should prove useful in this respect. In particular, it may be used to make a rough estimate of the induced hyperfine fields in an iron lattice of many nominally nonmagnetic atoms. For example, we may make the purely empirical observation that internal fields over $\sim 0.6\times 10^6$ G has been found only for elements with $Z>74$, for which all the seven measured fields are in excess of this figure (the rare earths, which are magnetic elements, should provide several exceptions to this observation, as discussed below).

The CEP estimates proposed here are oversimplified, and it would be wrong to over-emphasize the quantitative aspects of these estimates. The agreement with experiment of the internal fields predicted on this model lends some support to its validity. Of course the agreement may be only accidental and the large observed fields that we attribute to CEP may arise largely from CP. There is at present no feasible straightforward experimental technique for distinguishing between these two mechanisms. Because of the Pauli principle it must be "easier" for the unpaired spins of Fe to polarize, for example, the unfilled 6s shell of Au than to polarize the paired core s electrons (of course the inner s electrons have much higher probabilities of being in the nucleus—$\Psi_{ns}^2(0)$ increases about an order of magnitude for each unit decrease in n—and can create much larger hyperfine fields than can the 6s electron. The greater difficulty of polarizing the inner s electrons should offset even this factor). Certainly any mechanism which enables the Fe

[12] P. H. Barrett, R. W. Grant, M. Kaplan, D. A. Keller, and D. A. Shirley, J. Chem. Phys. **39**, 1035 (1963).
[13] R. W. Grant, Morton Kaplan, D. A. Keller, and D. A. Shirley, Phys. Rev. **133**, A1062 (1964).

electron spins to polarize the inner s electrons of Au must also produce substantial CEP via the $6s$ electrons. It should be noted that it is very important whether or not the impurity's d shell is polarized. The expectations of CP rise substantially if impurity d-shell polarization is present, as opposed to the case in which only the d shells (bands) of the host are polarized. We note that in the cases for which CP is experimentally well-established (the $3d$ group and the $4f^7$ configurations, Eu^{2+} and Gd^{3+}) this mechanism contributes only 500 kG or less to the hyperfine field of the atom in which several d or f electrons are unpaired. We thus feel that it is very unlikely that CP could be the dominant mechanism for Au in Fe and that the present evidence favors CEP for the heavy elements discussed above as well as for Ag in Fe (probably CP is also important for Ru in Fe). The relatively small fields for In, Sn, and Sb in Fe are also consistent with CEP. If this model is correct it should be useful in predicting internal fields. The following predictions can be made unambiguously:

1. The internal fields for Ir and Re should be negative.[14]

2. The internal fields for alkalies in Fe should be relatively small and negative. For Cs in Fe, the field should be approximately -150 kG. It is hard to make a quantitative estimate even on this simple model, because the alkalies are very electropositive and it is to be expected that the outer s electron density of an alkali atom will be considerably lower at that atom in an iron lattice than in the free atom or even in the alkali lattice. The $6s$ electron of a Cs atom produces a hyperfine field only 10% as large as that of the $6s$ electron on a gold atom, however, and this effect should be reflected in a much smaller hyperfine field for Cs in Fe than for Au in Fe if CEP is an important contributor to the fields.

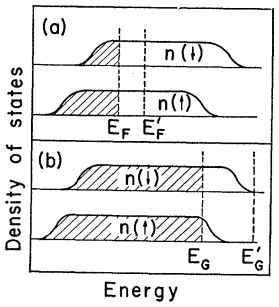

FIG. 4. Schematic density-of-states plots for polarized outer s electrons of (a) electropositive, (b) electronegative Group II atoms dissolved in a magnetic lattice. For alkaline earths [Fig. 4(a)] the outer electrons will be largely given to the host and the bands will not be very full. The nucleus will be relativly unshielded and the hyperfine field considerably larger than for the corresponding alkali atom. This prediction is comparatively straightforward because the internal field should not vary strongly with the exact location of the Fermi surface, E_F. For Group IIB atoms [Fig. 4(b)], the bands should be nearly full and the internal fields should be quite sensitive to the position of the Fermi surface. For the Fermi surface at E_G, for example, the spin polarization and hence the contact field, is large; for E_G', both are essentially zero.

[14] There is some experimental evidence that this is the case, but the conclusion is based on assumed nuclear magnetic moments. See A. V. Kogan, V. D. Kul'kov, L. P. Nikitin, N. M. Reinov, M. F. Stel'makh, and M. Schott, Zh. Eksperim. i Teor. Fiz. **43**, 828 (1962) [English transl.: Soviet Phys.—JETP **16**, 586 (1963)].

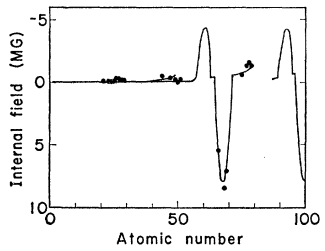

FIG. 5. Estimated internal fields for atoms dissolved in iron, versus atomic number. This is similar to Fig. 3, but the scale is much larger and the $4f$ and $5f$ groups are included, as discussed in text. The curves are based on the assumption that the $3d$ electrons of iron polarize the rare-earth $4f$ electrons by ferromagnetic *spin* polarization through the conduction s electrons. Measured fields at rare-earth nuclei in the Laves-phase intermetallic compounds Fe_2Dy, Fe_2Er, and Fe_2Tm are shown. Crystal-field effects could decrease the magnitudes of the hyperfine fields, especially in the lighter rare earths.

3. The hyperfine fields for alkaline earth atoms (Group IIB) in iron should be negative and substantially larger in magnitude than those of the corresponding alkalies. The alkaline earths are also quite electropositive, and the $6s$ shell (band) of a Ba impurity in Fe should not be nearly full, leading to a relatively unshielded Ba nucleus and thus a larger hyperfine field at the Ba nucleus. Thus the hyperfine field should increase abruptly, by about a factor of 2, from Cs in Fe to Ba in Fe. This point is illustrated in Fig. 4(a). A similar situation obtains for the free atoms (Table II), but for a different reason. To obtain the hfs constant a_{6s} for the Ba atom, it is necessary to observe configurations in which only one $6s$ electron orbital is filled. The other electron outside the xenon core must be in a higher orbital, where it can provide relatively little shielding.

For the more electronegative Group IB impurities (Zn, Cd, Hg), the CEP hyperfine fields are very sensitive to the amount of electron transfer from the host [Fig. 4(b)], and it is not possible to make an unambiguous estimate of the CEP field on the simple model described above. For the rare earths and actinides in iron the $4f(5f)$ shells will probably remain intact and produce the usual hyperfine fields characteristic of rare earths. If the atomic moments of these atoms are oriented in an iron lattice by spin-exchange polarization[15] one might expect large negative internal fields in the first half of the $4f(5f)$ shell and positive fields in the second half. We have worked out the expected internal fields, using the expression given by Elliott[16]

$$\mathbf{H}_N = 2\langle r^{-3}\rangle \beta N \langle \mathbf{J} \rangle . \qquad (2)$$

These fields are plotted in Fig. 5. Also plotted are ex-

[15] R. E. Watson and A. J. Freeman, Phys. Rev. Letters **6**, 277 (1961).

[16] R. J. Elliott, Rev. Mod. Phys. **36**, 385 (1964).

perimental points for the hyperfine fields at the rare-earth nuclei in Fe_2Dy,[17] Fe_2Er,[18] and Fe_2Tm.[19] Of course these are intermetallic compounds rather than dilute substitutional solid solutions, and thus not quite comparable to the other data. If cubic crystal field effects are important the fields given by Eq. (2) can be regarded only as upper limits.

[17] E. Bauminger, L. Grodzins, and A. J. Freeman, Rev. Mod. Phys. **36**, 392 (1964).
[18] R. L. Cohen and J. H. Wernick, Phys. Rev. **134**, B503 (1964).
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Antiferromagnetic Structure of Dysprosium Aluminum Garnet*

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The low-temperature antiferromagnetic structure of $Dy_3Al_5O_{12}$(DAG) has been established by means of neutron diffraction. The spin arrangement consists of six interpenetrating substructures directed along $\pm X$, $\pm Y$, $\pm Z$, as predicted by Wolf and co-workers. The observed value of the Dy^{+3} moment is $9.0\pm0.5\ \mu_B$, in agreement with the g value obtained from esr measurements.

INTRODUCTION

In a series of elegant papers, Wolf and co-workers[1–4] have presented evidence that dysprosium aluminum garnet (DAG) behaves like a three-dimensional Ising antiferromagnet in which dipolar forces account for more than half of the interaction energy.

Electron-spin-resonance measurements[1] on Dy^{+3} in yttrium aluminum garnet have shown that the general form of the spectrum is that of a Kramers-doublet ground state. This reduction to an effective spin of $s'=\frac{1}{2}$ is caused by crystal-field effects. The measured g values below 4°K are highly anisotropic with $g_\perp\approx0$ and $g_\parallel\approx18.2$, where the parallel axis refers to one of the three cubic axes depending on the location of the ion in the unit cell. Specific heat and susceptibility measurements on DAG indicated a transition to an antiferromagnetic state at $T_N=2.49$°K. Whereas no resonance can be obtained for Dy^{+3} in pure DAG, the expected similarity in the crystal field leads one to suppose that the ionic g tensor will be the same as in the dilute solid solutions and that, in the antiferromagnetic state, DAG can be regarded as a three-dimensional Ising model; i.e., three orthogonal, interpenetrating substructures of Ising spins. Assuming that the dominant ordering forces are magnetic dipole interactions, Wolf and co-workers[2–4] have been able to account for the susceptibility and specific heat measurements semiquantitatively.

The magnetic structure[1] assumed in computing the susceptibility below the Néel temperature was the one having the lowest dipolar energy subject to the condition of cubic symmetry. This structure is shown in

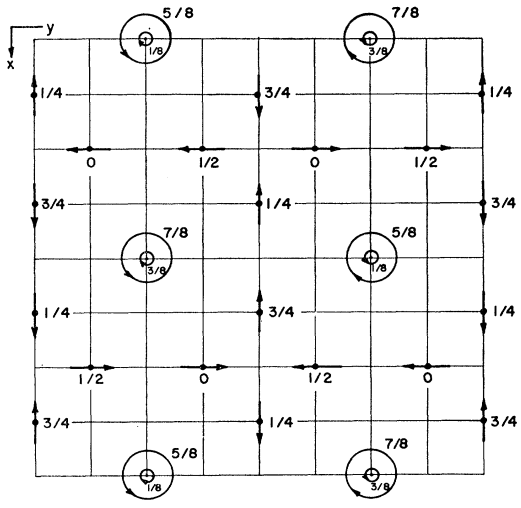

FIG. 1. Spin arrangement in DAG. Dy^{+3} ions are in special positions 24(c) of space group Ia3d. The numbers in the figure give the height above the $Z=0$ plane. Spins pointing along the Z axis are indicated as current loops in a right-hand sense.

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[1] M. Ball, M. T. Hutchings, M. J. M. Leask, and W. P. Wolf, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962* (Butterworth Scientific Publication, Ltd., London, 1963).
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[3] M. Ball, W. P. Wolf, and A. F. G. Wyatt, J. Appl. Phys. **35**, 937 (1964).
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