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HYPERFINE FIELD IN METALS AND ALLOYS

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Résumé. — On passe en revue les différentes contributions au champ magnétique au noyau dans les métaux et les alliages ferromagnétiques et paramagnétiques. La comparaison avec les résultats expérimentaux montre la faiblesse de la théorie, ainsi l'approche empirique du sujet est pour l'instant la meilleure méthode possible. Néanmoins les mesures de champ hyperfines peuvent fournir des reformations utiles. Par exemple, en utilisant l'effet Mossbauer — qui permet d'observer des distributions de champs trop larges pour être visibles en RMN — on peut en principe obtenir des informations sur les systèmes magnétiques désordonnées qui ne sont fournis par aucune autre technique.

Abstract. — A review is given of the contributions to the magnetic field at nuclei in ferromagnetic and paramagnetic metals and alloys. Comparison with experimental data shows the weakness of the theory and hence an empirical approach to the subject is the best possible at the present time. Nevertheless hyperfine field measurements may give useful information. For example using the Mossbauer effect, where distributions of fields too broad to be seen by NMR can be observed, information on random magnetic assemblies which cannot be obtained by any other technique may in principle be investigated.

The effective magnetic field acting on a nucleus in a solid can be discussed in various ways but it is best to regard it as the sum of the following contributions [1].

(a) The usual internal field which, for cubic materials, is

$$H_{\text{int}} = H_0 - DM + (4\pi/3) M \quad (1)$$

where H_0 is the external field, $-DM$ the demagnetising field and $4\pi M/3$ the Lorentz field. The Lorentz term has the coefficient $4\pi/3$ only in cubic symmetry but in all cases, even in crystals of low symmetry, H_{int} is known exactly. In paramagnetic metals H_{int} is the main field but in ferromagnets it is important only because the application of an external field H_0 of known sign enables the sign of the effective hyperfine field to be determined.

(b) The field produced by the orbital magnetic moment on the parent atom

$$H_{\text{L}} = -2\mu \langle r^{-3} \rangle \langle L \rangle \quad (2)$$

where μ is the Bohr magneton and the expectation values refer, for example to the $3d$ electrons of a transition metal or the $4f$ electrons of a rare earth metal.

(c) The field produced by the dipolar interaction with the spin moment on the parent atom

$$H_{\text{D}} = -2\mu \langle 3r(S \cdot r) r^{-5} - S r^{-3} \rangle.$$

In a cubic metal in the absence of spin orbit coupling this field is zero and if the crystal is non-cubic then the resulting field may very well be small enough to be neglected for most purposes. In the rare earth metals, however, because L is not quenched the electron density can have an asym-

metrical shape with a principal axis given by the S vector. In that case (3) can be quite large.

(d) The field proportional to the spin density at the nucleus.

$$H_{\text{s}} = - (16\pi/3) \mu \langle \sum_i s_i \delta(r_i) \rangle. \quad (4)$$

This field arises through the well known Fermi contact interaction.

The relative importance of these contributions varies from one type of material to another and it is therefore convenient to discuss the field under two headings: (1) ferromagnetic metals and alloys of the first transition period; (2) paramagnetic metals and alloys of the first transition period. We shall see that the problem of interpretation which arise are essentially similar and that we may therefore regard measurements of the hyperfine field in ferromagnets using, say, the Mössbauer technique as the equivalent of Knight shift measurements by N. M. R. in the paramagnetic materials. In contrast to these cases there are very few difficulties of interpretation connected with the rare earth metals and therefore we shall not discuss them.

1. Ferromagnetic métaux et alliages. — In these materials experiment shows that the effective field is large, usually of the order of several hundred kilogauss, and usually is negative. Therefore H_{int} is of little importance except to establish the sign of the field. The orbital term H_{L} is more conveniently expressed as

$$H_{\text{L}} = -2\mu \langle r^{-3} \rangle (g - 2) \langle S \rangle \quad (5)$$

and, because g is close to 2 in these materials, is

small compared to the total. Using a typical value of $g - 2 \sim 0.1$ we find H_L is of the order of $+70$ kg in Fe. Experiment on Fe shows that the total field is -340 kg [2] and hence, since H_D is zero for Fe, a field of the order of -410 kg must come from the spin density at the Fe nucleus. But before discussing this term in detail we first comment that H_D is not zero in hexagonal Co.

In a crystal with axial symmetry, such as hexagonal Co (3) can be put in the form

$$H_D = -2\mu \langle S \rangle \langle r^{-3} \rangle \langle 3 \cos^2 \theta - 1 \rangle \quad (6)$$

where θ is the angle between the spin direction and the principal axis. The best way to estimate this term is to measure the quadrupole interaction

$$H_Q = \frac{e^2 qQ}{4I(2I-1)} [3I_z^2 - I(I+1)] \quad (7)$$

where $q = 2 \langle r^{-3} \rangle \langle 3 \cos^2 \theta - 1 \rangle |\langle S \rangle|$. Hence H_D is simply μq . In this way G. Perlow [3], who has measured the quadrupole splitting of ^{57}Fe dissolved in hexagonal Co using the Mossbauer effect, concludes that H_D is smaller than 3 kg in this case. We conclude that even in an anisotropic crystal like hexagonal Co that nevertheless the electrons are distributed around the nucleus with a high symmetry and so H_D is in practice, quite negligible.

It follows that the hyperfine field in a ferromagnet is almost entirely due to the spin density at the nucleus. This is a well defined quantity but is difficult to interpret because our knowledge of these metals and alloys is poor and our understanding of how spin density is produced at the nucleus is weak.

In paramagnetic salts the mechanism by which a magnetic moment of the $3d$ electrons could give rise to a spin polarization at the nucleus has been understood in principle for some time. In physical terms the mechanism arises because the exchange interaction between the polarized $3d$ electrons and the inner core s electrons, $1s$, $2s$ and $3s$, produces an asymmetry between the inner electrons depending upon their spin orientation; and because of this asymmetry the inner core electrons can give a net spin density which, though zero on average, can have a non-zero value at the nucleus. A good formulation of the problem and a description of the calculations which it would be necessary to carry out was given by Abragam, Horowitz and Pryce [4]. They regard the problem as one of performing the appropriate configuration interaction calculation. To illustrate their argument let us consider the simple three electron case of Li where the Hartree-Fock wavefunction for the first excited state would be written as

$$\Psi_{\text{H.F.}} = \{ 1s_\beta 1s_\alpha 2p_\alpha \} \quad (8)$$

where the brackets $\{ \}$ stand for a properly norma-

lised determinant. The spin density at the nucleus is zero according to (8) because the $1s$ orbitals have paired spins and $2p$ orbital has zero amplitude at the nucleus. But to improve on the Hartree-Fock wavefunction we must add other configurations and Abragam, Horowitz and Pryce point out that the configuration where one of the $1s$ electrons is promoted into some higher state, R_s , is specially important for a discussion of spin density. They therefore took a wavefunction of the form

$$\Psi = \Psi_{\text{H.F.}} + \{ 1s_\beta R_{s_\alpha} 2p_\alpha \} + \{ 1s_\alpha R_{s_\beta} 2p_\alpha \} - 2 \{ 1s_\alpha R_{s_\alpha} 2p_\beta \} \quad (9)$$

where the function R_s is to be determined by a variational calculation and the precise form of (9) is dictated by the requirement that the total spin S^2 be a good quantum number. The wavefunction (9) does give a spin density at the nucleus which is $2 1s(0) R_s(0)$.

Unfortunately calculations of this type are difficult to perform and therefore many calculations have been made (e.g. by Freeman and Watson [5]) using the Unrestricted Hartree-Fock method which simply assumes a wavefunction of the type (8) with the radial form of $1s_\beta$ different from that of $1s_\alpha$. This method is simple but does not give eigenstates of S^2 and is therefore open to criticism. Some discussion of the validity of the Unrestricted Hartree-Fock method has been given by Marshall [6] but no clear decision seems possible at the present time. In view of this we should regard the Unrestricted Hartree-Fock method as a heuristic method capable of indicating trends and orders of magnitude: this point of view has been emphasised by Watson and Freeman themselves.

In principle it is clear that the same mechanism can give rise to core polarization in metals but because the " $3d$ electrons" are described by different wavefunctions in the metal it is impossible to make any estimate whether the effect is increased or decreased in metals. No calculations have yet been performed on anything other than isolated ions but Watson and Freeman have shown the effect is remarkably sensitive to the extent of the $3d$ radial function.

One point of importance upon which we do not even have qualitative information is the relative importance of $3d$ and $4s$ magnetisations in producing core polarization. In a ferromagnet such as Fe we can expect a $4s$ magnetisation of the order of 0.1 to 0.2μ per atom (it may well be negative) and we have no assessment of the core polarization this would produce.

Although core polarization probably provides the bulk of the hyperfine field in ferromagnetic metals a further contribution must also be made directly by the $4s$ conduction electrons. These electrons are polarized by both by the exchange

interaction with the $3d$ electrons (a positive term) and by the complicated effects of mixing with the $3d$ band. These mixing effects have been described by Anderson [7] but without a firm idea of the band structure of these metals it seems impossible to make a quantitative estimate of them.

Another difficulty is that the spin density even in a free electron gas can be very non-uniform. This has been studied by Yosida [8] who has pointed out that in some cases the spin density can fluctuate from one part of the unit cell to another by an order of magnitude more than the mean value.

This suggestion is borne out by the experiments of Gossard, Jaccarino and Wernick [9] on the Laves phases RAI where R is a rare earth atom. They find that the Knight shift at the aluminium nucleus is negative although the exchange effect between the rare earth ions and the conduction electrons is certainly positive.

This point of great importance is considering the results on the hyperfine fields of diamagnetic atoms dissolved in a ferromagnet. Many measurements of this kind have been made and some of the data are summarised in Table I, together with

TABLE I

Nucleus/Host	H (10^6) gauss			$\langle S \rangle$		
	Fe	Co	Ni	Fe	Co	Ni
^{27}Al	σ .17	—	—	0.105	—	—
^{63}Cu	0.213	0.158	—	0.081	0.060	—
^{114}In	0.25	—	—	0.072	—	—
^{119}Sn	— 0.088	— 0.026	+ 0.016	+ 0.0255	+ 0.0078	— 0.0046
^{122}Sb	(+) 0.280	—	0.1	—	—	—
^{197}Au	+ 1.46	1.18	0.53	— 0.034	0.27	0.012

Note that H and $\langle S \rangle$ are of opposite signs.

The sign of H is most directly determined in Mössbauer measurements (e.g. ^{119}Sn , [18] ^{197}Au) [19], Samoilev et al deduce sign the from the asymmetry of β -emission from oriented nuclei. They obtain negative fields for ^{198}Au in Fe and Ni [20]. The positive sign for ^{122}Sb is not yet definite.

The relative values of H for ^{197}Au in Fe, Co and Ni are known more accurately than the absolute values, and are proportional to the saturation magnetisation (Roberts and Thomson [10]). The positive sign has been measured by Shirley and al. [19].

The data for ^{27}Al and ^{63}Cu were obtained by Koi et al. [21].

estimates of the spin of the conduction electron in the impurity unit cell calculated on the assumption that for the diamagnetic atom the entire field comes from a Knight shift effect via the conduction electrons. We notice that the mean spin values required to fit the experimental data vary widely from one atom to another both in magnitude and sign, and in view of the expected fluctuations in the spin density this is not surprising. [However Roberts and Thomson [10] find that the hyperfine field on ^{197}Au dissolved in iron cobalt and nickel is accurately proportional to the saturation magnetisation of the specimen.]

In trying to interpret hyperfine fields measured for magnetic atoms the unsatisfactory understanding of the theory reduces us to trying to fit the data to empirical rules. The simplest rule we could postulate is that the field should be proportional to the magnetic moment on the atom. For some ordered alloys this rule appears to hold ; for example in the ordered alloy Fe_3Al there are two ion sites whose hyperfine fields [11] and atomic moments [12] are

H (kilogauss)	μ (Bohr magnetons)	H/μ
295	2.16	137
212	1.46	145

The value of H/μ for pure ion is 150, which agrees well with the last column above. However, such agreement appears to be confined to isolated examples.

Figure 1 shows the variation of the hyperfine field at ^{57}Fe nuclei as a function of composition in iron alloys with cobalt, nickel, chromium, vanadium and aluminium [11]. Also shown are the magnetic moment μ_{Fe} localised on the iron atoms (determined from diffuse scattering of neutrons [13] or from the saturation magnetisation for $Fe-Al_1$ where the aluminium contributes no moment) and the average atomic moment μ (determined from saturation magnetisation measurements). The three quantities H_{Fe} , μ_{Fe} and μ have been normalised in terms of the values for pure iron : It is clear that the simple rule does not hold in general. In all these cases it is observed that the hyperfine field varies with alloys concentration in a way which is intermediate between that of the iron moment itself and the mean moment of the sample as a whole. However, no solution of the form $H_{Fe} = a\mu_{Fe} + b\mu$ with constant a and b can be found to fit all the alloys. Part of the discrepancies may be accounted for the changes in the number of conduction electrons with alloy composition. For example in the $Fe-Al$ system the

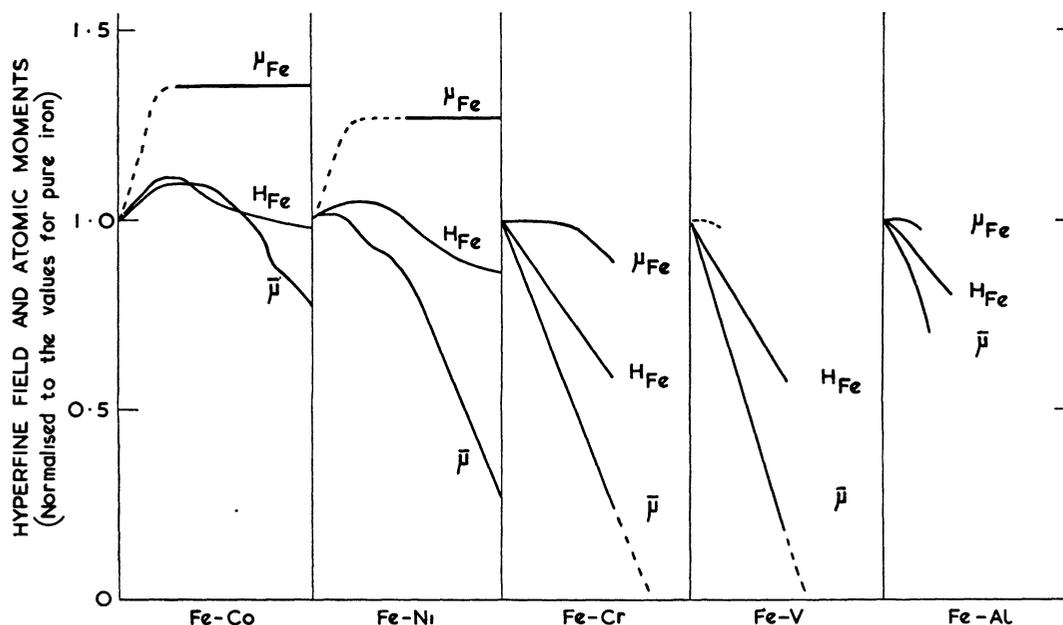


FIG. 1. — The variation of the hyperfine field as iron nuclei H_{Fe} , the magnetic moment on iron atoms μ_{Fe} and the average magnetic moment $\bar{\mu}$ for iron alloys. Values are normalised to those of pure iron.

Mössbauer spectrum shows a positive isomer shift with increasing aluminium content [11] corresponding to a decrease in the number of conduction electrons and hence a more rapid fall in the hyperfine field than that expected for a decrease in μ alone. Another result of alloying which may affect the hyperfine field is a change in the density of states, which may be inferred from the linear contribution to the low temperature specific heat. Perhaps when more complete data for alloys becomes available, an empirical law may be found which takes into account the changes in electronic structure which accompany alloying.

Even though detailed interpretation of the hyperfine field data is not yet possible, these measurements can be of value in studying the magnetic properties of atoms in different environments in alloys. As an example the two iron sites in ordered Fe_3Al have already been cited. Hyperfine field measurements using the Mössbauer effect might be used to test the model which has been postulated by Marshall [14] for antiferromagnetism in dilute alloys. According to this model there is a distribution $p(H_e)$ of local magnetic fields H_e at the magnetic atoms such that $p(0)$ is not zero, i.e. there is a finite probability that atoms will be situated in a region of zero or small fields. These spins are free to change their orientation and hence give rise to a specific heat at low temperatures. Since they are free to flip they have $\langle S \rangle = 0$ and no hyperfine field. The spins in large local fields are locked to the crystal and would be expected to show a normal hyperfine field. Hence the

Mössbauer spectrum of such an antiferromagnet would show a spread in hyperfine fields, and in particular an appreciable number of nuclei should be in small fields resulting in an unsplit line in the centre of the spectrum. The lower the temperature the fewer spins contribute to this centre line and so in principle by measuring its intensity as a function of temperature the distribution function $p(H_e)$ could be determined. Beck [15] has made the interesting suggestion that anomalies in the linear term in the specific heat of more concentrated disordered alloys may arise from a similar mechanism involving a distribution of local fields acting on the atoms.

2. Paramagnetic metals and alloys. — In these materials the main contribution is H_0 , the magnetisation M is small and the small terms additional to H_0 give the Knight shift. We recognise that there are the following contributions to the Knight shift which we shall roughly evaluate for the case of vanadium. The polarization of the $4s$ conduction electrons, acting through (4), gives the well known result [16]

$$H_s = (8\pi/3) |\Psi(0)|^2 \chi_s H_0 \approx 15 \times 10^{25} \chi_s H_0 \quad (10)$$

where χ_s is the Pauli susceptibility of the conduction electrons and $|\Psi(0)|^2$ is averaged over the Fermi surface and, in principle, includes the effects of core polarization produced by polarization in the $4s$ electrons. The $3d$ electrons are also polarized by the external field and this produces a core polarisation and hence a core field of

$$H_c = (\alpha/\mu) \chi_d H_0 \approx 10^{25} \chi_d H_0 \quad (11)$$

where α is the field produced by one Bohr magneton in the $3d$ electrons and is therefore very roughly of the order of 100 kg. Finally we notice that we expect a van Vleck susceptibility [17] χ_{VV} of the order of $(2\mu^2/5\Delta)n(10-n)$ and this leads to a field, through (2), of

$$H_{\text{L}} = (\mu^2 n/\Delta)(10-n) \langle r^{-3} \rangle_{3d} H_0 \quad (12)$$

where Δ is an energy parameter of the order of the width of the $3d$ band and n is the number of $3d$ electrons per atom. Because $\mu^2 n/\Delta$ is of the order of χ_d and $\langle r^{-3} \rangle_{3d}$ is about $3 \times 10^{25} \text{ cm}^{-3}$ it follows that H_{L} is of the same order and may very well be longer than H_c . The numerical results quoted in (10), (11) and (12) are only rough but because we can expect χ_d to be an order of magnitude larger than χ_s we conclude that in general all three contributions are very roughly comparable. We should however specially emphasize the difficulties of estimating (11) and (12): we have

previously pointed out the weakness of our understanding of core polarization in metals and the estimate of the Van Vleck susceptibility is also very difficult because it depends sensitively on the detailed band structure of the metal.

We conclude that the proper interpretation of Knight shifts in these metals is very hard indeed. The same remark applies to measurements of the nuclear spin relaxation rate, $1/T_1$. There are three contributions to this relaxation rate corresponding to the three contributions to the Knight shift we labelled H_s , H_c and H_{L} ; in addition there is a fourth contribution, of the same order, which has its origin in the dipole interaction with the $3d$ electrons. This dipole interaction can contribute to scattering and hence to $1/T_1$ but not to the Knight shift in cubic materials. Notice that for S -like conduction electrons alone this dipole relaxation rate is unimportant because $\langle r^{-3} \rangle_{4s}$ is very much smaller than $|\Psi_{4s}(0)|^2$.

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