NMR evidence for a transferred orbital hyperfine field on near neighbours of Fe in Cu

H. Alloul, H. Ish

► To cite this version:

H. Alloul, H. Ish. NMR evidence for a transferred orbital hyperfine field on near neighbours of Fe in Cu. *Journal de Physique Lettres*, 1977, 38 (22), pp.449-453. 10.1051/jphyslet:019770038022044900 . jpa-00231418

HAL Id: jpa-00231418

<https://hal.science/jpa-00231418>

Submitted on 1 Jan 1977

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

LE JOURNAL DE PHYSIQUE-LETTRES

Classification
Physics Abstracts
76.60C — 75.20H

NMR EVIDENCE FOR A TRANSFERRED ORBITAL HYPERFINE FIELD ON NEAR NEIGHBOURS OF Fe IN Cu

H. ALLOUL and H. ISHII (*)

Laboratoire de Physique des Solides (**),
Université Paris-Sud, 91405 Orsay, France

(Reçu le 8 septembre 1977, accepté le 19 octobre 1977)

Résumé. — A partir de spectres obtenus sur des poudres de CuFe (de 1,4 K à 300 K) on démontre que l'anisotropie de la RMN des Cu voisins du Fe observée à 300 K par Stakelon et Slichter sur des échantillons monocristallins ne peut pas être expliquée par un couplage pseudodipolaire. Les expériences révèlent l'existence de contributions indépendantes de la température aux champs locaux isotrope et anisotrope. Un calcul de la polarisation de spin induite par l'aimantation orbitale de l'impureté par l'intermédiaire du couplage spin orbite permet d'expliquer en ordre de grandeur les résultats expérimentaux.

Abstract. — Satellite NMR data taken on CuFe powders (from 1.4 to 300 K) show that the anisotropy deduced by Stakelon and Slichter from single crystal experiments at 300 K cannot be explained by a pseudodipolar coupling. Temperature independent contributions to both the isotropic and anisotropic parts of the local field tensor are evidenced. A calculation of the spin polarization induced by the impurity orbital magnetization through spin orbit coupling gives an order of magnitude agreement with the data.

The physical properties of 3d impurities in noble metal hosts have in most cases been explained in terms of the sd or degenerate Anderson models [1]. For example, in the well known CuFe Kondo system, various hyperfine studies have demonstrated that the static [2-5] and dynamic *spin susceptibilities* [6] of Fe do behave qualitatively as would be expected from exact solutions of the sd and Anderson models [7]. Although crystal field and spin orbit coupling have usually been neglected, it is clear that these effects must be taken into account in order to explain some detailed hyperfine measurements, e.g. those linked with the impurity *orbital susceptibility* [8]. In some cases, like W-Co [9] or Au-Co [10] an ionic description [11] of the impurity states is even needed to account for the unusual NMR properties of these alloys.

In CuFe and CuCo Stakelon and Slichter [12] (S. S.) have measured the Knight shift tensors for some near neighbour (n.n.) shells of the impurity. They associated the anisotropic part of the n.n. NMR shifts with the dipolar (D) and pseudodipolar (PD) couplings of the nuclear spin I with the impurity spin magnetization $\langle S_z \rangle$. The observed asymmetry of the Knight

shift tensors for some of the neighbour shells are clearly linked with crystal field effects. Using this information Boyce and Slichter [2] (B. S.) conjectured that the shape of the spin polarization in CuFe reflects the splitting of the impurity virtual bound states (vbs) by the crystal field.

In order to get further insight into the significance of these results we have obtained n.n. NMR data on CuFe at low T which demonstrate that the anisotropic local fields observed by S.S. at 300 K do not scale with $\langle S_z \rangle$ and cannot therefore be associated solely with D and PD couplings. We propose the presence of a local field on the host site induced by the impurity orbital magnetization through the spin orbit coupling and which can account for the T independent contribution to the measured local fields. To our knowledge this is the first experimental evidence for the existence of a transferred orbital hyperfine field in dilute Kondo alloys.

Ideally single crystal experiments allow the most accurate determination of the local field tensor on a n.n. shell of an impurity. However the width of the satellite resonances in powder samples are found to increase greatly at low T [2, 4]. This line broadening might smear the complicated spectra expected for a given n.n. shell NMR, in single crystal experiments. Boyce and Slichter have suggested that the spin

(*) On leave from the Department of Physics, Osaka City University, Japan.

(**) Laboratoire associé au C.N.R.S.

lattice relaxation T_1 induced by the impurity was responsible for this line broadening. However our direct measurements of T_1 [4, 6] show that this effect is quite negligible. The large concentration dependence of the linewidth ΔH observed on the 3rd n.n. of Fe (Fig. 1) rather demonstrates that a large part of the satellite broadening is associated with the distribution of impurity susceptibilities due to interactions between impurities. However the large finite linewidth ΔH_0 (much greater than the pure dipolar

FIG. 1. — NMR half intensity width ΔH of the 3rd n.n. ^{63}Cu satellite resonance (B) versus ΔK (i.e. temperature) and impurity concentration, taken at 58 MHz. The single impurity limit ΔH_0 is obtained by extrapolation to zero concentration.

width ~ 8 G) obtained by extrapolation to zero concentration is associated with the angular distribution of anisotropic local fields induced by single impurities. The measured ΔH_0 at $T \sim 300$ K is in good agreement with the anisotropy measured by S. S. on this satellite (B), but it can be seen that ΔH_0 does not scale with the isotropic shift ΔK , that is with the spin magnetization $\langle S_z \rangle$. In order to clarify this point, spectra for B and M (2nd n.n.) in a low concentration sample (20 ppm) have been recorded at 1.4 K and are displayed in figure 2. For such a concentration, interactions between impurities only yield a very small broadening (~ 60 G), and therefore most of the satellite structures should be associated with a powder spectrum of the anisotropic local fields. While M has a clearcut anisotropic shape, B is nearly isotropic and narrower than M. This situation is exactly opposite to that found by S. S. at 300 K, as no anisotropy could be detected by these authors for the satellite M. The powder spectra expected from the $T = 300$ K local field tensors, assuming a D and PD origin for the local fields are also shown on figure 2 for comparison. As suggested by figure 1 it can then be concluded that a T independent contribution to the anisotropy has to be added to the usual D and PD terms.

FIG. 2. — Recorded spectra for satellites B and M, taken at 1.4 K and 58 MHz on a CuFe 20 ppm sample. The powder pattern spectra expected from the single crystal data taken at 300 K by Stakelon and Slichter [12] assuming a D + PD origin for the anisotropic local field are shown for comparison with the same integrated intensity. The values for K_{zz}/K are then obtained from those of S.S. at 300 K by scaling with ΔK . The concentration dependent part of the broadening in this sample is smaller than 60 G in both cases.

As powder spectra cannot allow complete determinations of the local field tensor, we assume that this tensor has an axial symmetry around one of its principal axes z . This simplification, which makes possible order of magnitude estimates allows us to write the anisotropic local field ΔH_{ax} for a given site :

$$\Delta H_{ax}/H = K_{zz}(3 \cos^2 \theta_z - 1)/2 \quad (1)$$

where θ_z is the angle between the external field H and z , and K_{zz} characterizes the strength of the anisotropy. A good estimate for K_{zz} for M is obtained by fitting the line of figure 2 with a powder spectrum for eq. (1).

Although the existence of a small hump on the high field site of satellite B might indicate that K_{zz} is negative at 1.2 as well as at 300 K, [12] the sensitivity is not high enough to verify this point. However the monotonic T dependence of ΔH (and ΔH_0) for this satellite, from 1.2 K to 300 K indicates that no change of sign of K_{zz} occurs in this temperature range (which would imply a minimum at the temperature for which K_{zz} vanishes). The estimated values for K_{zz} then allow an analysis of the T dependence of the anisotropy to be made assuming that :

$$K_{zz}/K = \alpha(\Delta K/K) + \beta, \quad (2)$$

TABLE I

Anisotropic shift K_{zz} for satellites B and M measured at $T = 300$ K and $T = 1.4$ K, and values for α and β deduced from eq (2). α_d is the pure dipolar term

	K_{zz}/K $T = 300$ K	K_{zz}/K $T = 1.4$ K	$\Delta K/K$ $T = 1.4$ K	β	α	α_d
B						
3rd n.n.	-0.29 ± 0.05	-0.70 ± 0.20	-13.73 ± 0.1	-0.24 ± 0.08	$+0.035 \pm 0.020$	-0.06
M						
2nd n.n.	$0. \pm 0.05$	1.88 ± 0.30	22.8 ± 0.3	-0.16 ± 0.09	0.09 ± 0.015	0.073

where $K = 0.232\%$ is the pure Cu Knight shift. The results are summarized in table I together with the calculated purely dipolar value α_d for α . It can then be seen that the PD coupling has about the same order of magnitude as the pure dipolar coupling, but is not as large as concluded by S. S. Also β is an essential contribution at $T = 300$ K to the anisotropic local fields.

Finally knowing that both the macroscopic susceptibility and the ^{57}Fe Mössbauer local field data [3] show the existence of an orbital T independent contribution, we have searched for a similar effect on the isotropic shift ΔK . Accurate measurements of ΔK for satellite B above 77 K given in figure 3 allowed us to show that $\Delta K(T)$ does not follow a single Curie-Weiss law ($\propto (T + \theta)^{-1}$) at all T . For $100 < T < 350$ K, as can be seen in figure 3 the data corresponds to a value $\theta \sim 50$ K higher than that obtained from the susceptibility measurements ($\theta = 27.6 \pm 1.5$ K) [3]. The data can be analysed by assuming that $\Delta K/K$ is proportional to χ_{spin} , as was already shown at low T , apart for a constant term $\Delta K_0/K = -0.15 \pm 0.05$ which is obtained by extrapolation to $T \rightarrow \infty$ (Fig. 3 insert). It is therefore quite natural to associate all the T independent local fields with the orbital susceptibility χ_{orb} .

FIG. 3. — Inverse of the 3rd n.n. NMR shift ΔK versus T . It can be seen that $K/\Delta K$ does not follow a single Curie-Weiss law. At high T the best fit is obtained for $\theta \sim 50$ K. A better analysis of the data is shown in the insert where ΔK is assumed to scale with the spin susceptibility ($\propto (T + 27.6)^{-1}$) apart for a constant contribution ΔK_0 .

Assuming that H is applied along OZ, a general equation for the Z component of the local field H_{int} induced by an impurity, located at the origin O, on a host nucleus, at $\mathbf{R}$, is given by :

$$H_{\text{int}}^Z(\mathbf{R}) = A \langle \sigma_Z(\mathbf{R}) \rangle + 2 \mu_B \int [\langle S_Z \rangle \delta(\mathbf{r}) + \langle \sigma_Z(\mathbf{r}) \rangle] [\xi^{-3} - 3 \xi_Z^2 \xi^{-5}] d^3\mathbf{r} - 2 \mu_B \hbar^{-1} \int \langle \psi^+(\mathbf{r}) (\xi \times \mathbf{p}) r^{-3} \psi(\mathbf{r}) \rangle d^3\mathbf{r}, \quad (3)$$

where $\langle \sigma_Z(\mathbf{r}) \rangle$ is the spin polarization at $\mathbf{r}$, $\langle S_Z \rangle = \chi_{\text{spin}} H/g\mu_B$ is the induced impurity spin, A denotes the host hyperfine constant ($A \sim 3.3 \times 10^{-17}$ emu for Cu [13]), $\xi = \mathbf{r} - \mathbf{R}$, and $\psi(\mathbf{r})$ is the field operator which is a linear combination of d and s states for both spins. The second term of (3) contains both D and PD fields and the third is due to the orbital current (OC). We calculate (3) for the Anderson model with orbital degeneracy ($l = 2$) [14, 15].

$$H = \sum_{k\sigma} \varepsilon_k n_{k\sigma} + E_d \sum_{m\sigma} n_{m\sigma} + \sum_k V_k (c_{k\sigma}^+ a_{m\sigma} + a_{m\sigma}^+ c_{k\sigma}) + (U/2) \sum a_{m_1\sigma_1}^+ a_{m_2\sigma_2}^+ a_{m_2\sigma_2} a_{m_1\sigma_1} + (J/2) \sum a_{m_1\sigma_1}^+ a_{m_2\sigma_2}^+ a_{m_1\sigma_2} a_{m_2\sigma_1} - \sum_{m\sigma} (h_1 \sigma + h_2 m) a_{m\sigma}^+ a_{m\sigma}, \quad (4)$$

where $h_1 = g\mu_B H/2$, $h_2 = \mu_B H$. We can express $\langle \sigma_z(\mathbf{r}) \rangle$ in terms of d electron Green's functions $G_{m\sigma}$ as in ref. [5],

$$\langle \sigma_z(\mathbf{r}) \rangle = - \frac{2 E_F \Delta}{\pi^3 k_F^3} \sum_{\sigma} \sigma |Y_2^m(\hat{r})|^2 \text{Im} \int_{-\infty}^{+\infty} f(\omega) G_{m\sigma}(\omega^+) F_r^2(\omega^+) d\omega, \quad (5)$$

where

$$\omega^+ = \omega + i0^+, \quad f(\omega) = (1 + e^{\beta\omega})^{-1},$$

$$F_r(x) = \int_0^\infty dk k^2 j_2(kr)/(x - \varepsilon_k). \quad (6)$$

The last term of (3) can also be expressed in terms of $G_{m\sigma}$. In first order in H , $G_{m\sigma}$ is decomposed into two terms proportional respectively to $h_1 \sigma$ or $h_2 m$. The latter term vanishes in the summation in (5) and therefore $\langle \sigma_z(\mathbf{r}) \rangle$ only contains the isotropic RKKY term, which is proportional to χ_{spin} . An anisotropic term is only given by (OC) which yields as a dominant term $\chi_{\text{orb}} H(1 - 3 \cos^2 \theta_R)/R^3$, the dipole term due to the orbital moment of the impurity, which is too small to explain the experimental result. (Here θ_R is the angle between $\mathbf{H}$ and $\mathbf{R}$.) Therefore Hamiltonian (4) is not sufficient.

Including the crystalline field effect in fact yields an anisotropic spin polarization. However an analysis similar to eq. (5) shows that this anisotropy is linked with a difference of the Green's functions for the two spin directions and therefore with χ_{spin} . Furthermore this anisotropy is found to vanish on the lattice sites [16].

Finally let us consider the spin orbit coupling H_{so} on the impurity, which can connect χ_{orb} with $\sigma(\mathbf{r})$, and is actually the main source for conduction electron spin relaxation by the local moment [17] :

$$H_{\text{so}} = \lambda \sum_{mm'\sigma\sigma'} a_{m\sigma}^+ a_{m'\sigma'} \langle m\sigma | \mathbf{l} \cdot \mathbf{s} | m'\sigma' \rangle. \quad (7)$$

The key point is that any contribution to $G_{m\sigma}$ which is proportional to $m^2 \sigma$, will give, through eq. (5) :

$$\langle \sigma_z(\mathbf{R}) \rangle \propto \sum_{m\sigma} \sigma |Y_2^m(\hat{R})|^2 m^2 \sigma = (15/2 \pi) \sin^2 \theta_R.$$

Such a contribution is given by the cross term of the orbital Zeeman energy and the diagonal term of H_{so} . Since $\lambda \ll \Delta$ for iron group impurities, we consider H_{so} only in first order, for which spin flip parts of H_{so} give no contribution as the total spin is conserved by Hamiltonian (4). In order to allow a semi quantitative comparison with the experimental result, we calculate this part of eq. (5) in the Hartree-Fock approximation. Its asymptotic form can be easily obtained in terms of phase shifts at E_F , $\eta_\sigma = \pi \langle \eta_\sigma \rangle$ as

$$\langle \sigma_z^{\text{so}}(\mathbf{R}) \rangle = \frac{15 \lambda \mu_B H}{8 \pi^2 R^3 \Delta^2} \sin^2 \theta_R \sum_{\sigma} \alpha_{\sigma}^2 \sin^3 \eta_{\sigma} \times$$

$$\times [\alpha_{\sigma} \cos \eta_{\sigma} \cos (2 k_F R + 2 \eta_{\sigma}) - \sin \eta_{\sigma} \sin (2 k_F R + 2 \eta_{\sigma})] \quad (8)$$

with $\alpha_{\sigma} = [1 - \{(U - J)/\pi\Delta\} \sin^2 \eta_{\sigma}]^{-1}$. For the special case of electron-hole symmetry ($n_{\uparrow} = n_{\downarrow} = 1/2$), $\sigma_z^{\text{so}}(\mathbf{R})$ can be calculated exactly along the same lines as in ref. [5]. Its asymptotic form is given by the part of $G_{m\sigma}(0^+)$ proportional to λh_2 . The self-energy part of $G_{m\sigma}(0^+)$ can be represented in term of χ_{orb} using Yoshimori's method [15], if it is noticed that the diagonal term of H_{so} can be treated similarly to the orbital Zeeman energy term. Our result is written as :

$$\langle \sigma_z^{\text{so}}(\mathbf{R}) \rangle = \frac{3 \sin 2 k_F R}{16 \pi R^3} \sin^2 \theta_R \frac{\tilde{\lambda}}{\Delta} \frac{\chi_{\text{orb}} H}{\mu_B}, \quad (9)$$

where $\tilde{\lambda} = \lambda \chi_{\text{orb}}/\chi_{\text{orb}}$ ($U = J = 0$) is the enhanced spin orbit coupling. The HF result of eq. (8) reduces to the same form as eq. (9) when $n_{\uparrow} = n_{\downarrow} = 1/2$ as

$$\chi_{\text{orb}}^{\text{HF}} = (10 \mu_B^2/\pi\Delta) \sum_{\sigma} \alpha_{\sigma} \sin^2 \eta_{\sigma}.$$

It is then clear that such a process yields both isotropic and anisotropic local fields, as $\langle \sigma_z^{\text{so}}(\mathbf{R}) \rangle$ can be decomposed into $2 \sigma_A + \sigma_A(1 - 3 \cos^2 \theta_R)$. The magnitude of $\beta = -2 \Delta \sigma_A/HK$ can be estimated in the HF limit. Taking $5(n_{\uparrow} + n_{\downarrow}) = 7$, $S = 1.25$ for CuFe [13], it can be seen that the main contribution to σ_A as well as $\chi_{\text{orb}}^{\text{HF}}$ are given by the down spin component. Choosing the plausible values $\Delta = 0.5 \text{ eV}$, $(U - J)/\Delta = 2.5$, which gives

$$\chi_{\text{orb}}^{\text{HF}} = 1.4 \times 10^{-27} \text{ emu},$$

in good agreement with

$$\chi_{\text{orb}}^{(\text{exp})} = 1.3 \pm 0.3 \times 10^{-27} \text{ emu} \quad [3],$$

and $\lambda \simeq 400 \text{ cm}^{-1}$ [18] yields, from eq. (8),

$$\beta(\text{M}) = -0.78 \quad \text{and} \quad \beta(\text{B}) = 0.54.$$

As eq. (8) is an asymptotic form of $\langle \sigma_z^{\text{so}}(\mathbf{R}) \rangle$, the order of magnitude agreement with the data of table I is satisfactory.

Therefore the T independent contribution to both the *isotropic* and *anisotropic* local fields are associated with the indirect hyperfine coupling between the host nucleus and the impurity orbital magnetization through spin-orbit coupling. Such an effect can only be important when χ_{orb} becomes comparable to χ_{spin} i.e. for systems like CuFe and CuCo, and can therefore explain the large magnitude of the anisotropic local fields detected by S. S. in these systems. It is certainly negligible in CuMn for which $\rho_d(E_F)$ is small.

Apart from providing good order of magnitude explanation of the data, the numerical results presented here are of limited significance as crystal field has been neglected, and rather crude simplifications have been made in the calculation.

For instance eqs. (8) and (9) would imply

$$\Delta K_0/K = -\beta$$

while the data for B corresponds to $\Delta K_0/K \simeq +0.6\beta$, which is correct in order of magnitude but not in sign. Also the local field obtained in eq. (8) has the same

symmetry as the pure dipole field while S. S. found an asymmetry of the local field tensor, and have shown that θ_z does not coincide with θ_R , at least for satellite B in CuFe. Taking into account Bloch waves rather than plane waves to describe the s electrons might modify the angular dependence of eqs. (8) and (9) and introduce asymmetries of the local field tensor for some shells which have a low symmetry. Such modifications can also occur if a crystal field splitting of the impurity vbs is assumed. However in our opinion, taking these effects into account will not modify the main qualitative results of this paper concerning the T independent contribution to the transferred local fields. Similar effects are also expected for the PD coupling as suggested by S. S. However detailed knowledge of the PD tensors are not available at present but might be obtained from low T single crystal data in strongly magnetic systems such as CuMn, CuCr and CuFe. Comparison between these systems might indeed help to distinguish between the above mentioned possibilities and also help to determine the influence of the crystal field on the magnetic properties of transition metal impurities in copper.

References

- [1] Series of review articles on Kondo effect : *Magnetism*, G. T. Rado and H. Suhl Ed. (Academic Press, New York) **5**, 1973.
- [2] BOYCE, J. B. and SLICHTER, C. P., *Phys. Rev. B* **13** (1976) 379.
- [3] STEINER, P., HÜFNER, S. and ZDROJEWSKI, W. V., *Phys. Rev. B* **10** (1974) 4704.
- [4] ALLOUL, H., *Phys. Rev. Lett.* **35** (1975) 460, in *MMM* (1975), BECKER, J. J., LANDER, G. H. and RHYNE, J. J. (Ed. AIP, New York) 1976, p. 300.
- [5] ISHII, H., *Prog. Theor. Phys.* **55** (1976) 1373, *Physica* **86-88B** (1977) 517.
- [6] ALLOUL, H., *J. Physique Lett.* **37** (1976) L-205, *Physica* **86-88B** (1977) 449.
- [7] WILSON, K. G., *Rev. Mod. Phys.* **47** (1975) 773; KRISHNA-MURTHY, H. R., WILSON, K. G. and WILKINS, J. W., *Phys. Rev. Lett.* **35** (1975) 1101. NOZIERES, P., *Low. T. Phys. J.* **17** (1974) 31. YAMADA, K., *Prog. Theor. Phys.* **53** (1975) 970, **54** (1975) 316; YOSIDA, K. and YAMADA, K., *ibid.* **53** (1975) 1286.
- [8] NARATH, A., in ref. [1] chap. 5.
- [9] NARATH, A., *Phys. Rev. B* **13** (1976) 3724.
- [10] DUPREE, R., WALSTEDT, R. E. and WARREN, W. W. Jr., *Phys. Rev. Lett.* **38** (1977) 612.
- [11] HIRST, L. L., *Phys. Condens. Matter.* **11** (1970) 255, in *MMM* (1977), GRAHAM, C. D., Jr., LANDER, G. H. and RHYNE, J. J. (Ed. AIP, New York) 1975, p. 11.
- [12] STAKELON, T. S. and SLICHTER, C. P., *Phys. Rev. B* **14** (1976) 3793.
- [13] ALLOUL, H., DARVILLE, J. and BERNIER, P., *J. Phys. F* **4** (1974) 2050.
- [14] DWORIN, L. and NARATH, A., *Phys. Rev. Lett.* **25** (1970) 1287.
- [15] YOSHIMORI, A., *Prog. Theor. Phys.* **55** (1976) 67.
- [16] A complete discussion of this point will be given in a future publication.
- [17] YAFET, Y., *J. Appl. Phys.* **42** (1971) 1564.
- [18] BLUME, M. and WATSON, R. E., *Proc. R. Soc.* **271** (1963) 565.