CO adsorption parallel to the surface compared to CO perpendicular, raising the possibility that large level shifts might not unambiguously imply dissociation. (3) SCF eigenvalue spectra are found to be similar for a variety of theoretical treatments (d^3 localization, orthogonalization of s,p orbitals to localized d orbitals, mixing of s,p, and d electrons); however, these treatments differ greatly in total energy and CO binding energy. (4) For CO near the surface, particularly in the parallel stretched and dissociated cases, a strong field (Pauli principle plus electrostatic) exists such that occupied surface d orbitals either partially depopulate or rotate away from the occupied CO orbitals. (5) Large increases in the electronic populations of C and O p_π orbitals occur on CO bonding to Ti (often attributed to $d \rightarrow \pi^*$ backbonding); however, the principal sources of metal electrons are the 4s combinations of orbitals on different Ti atoms with the same symmetry as the C and O p orbitals; the charge transfer is further increased on the inclusion of d orbitals.

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Nuclear Magnetic Resonance on Brute-Force-Oriented ^{111}In

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With use of radiative detection, NMR was performed on "brute-force"-oriented ^{111}In implanted in copper by use of an electromagnetic isotope separator. A sharp resonance line was detected, in contrast with hyperfine-enhanced NMR on oriented nuclei. The deduced Knight shift of In in Cu is 0.65(11)%.

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The combination of nuclear orientation and NMR has led to a large number of new techniques and applications. In particular, the use of radioactive nuclei allows one to work in the limit of extreme dilution since the anisotropy of the emitted radiation can be used to detect the NMR signal. Although scientific interest in this combination was suggested by Bloembergen and Temmer already in 1953,[1] the first successful experiment of NMR on low-temperature-oriented ^{60}Co was not realized until 1966 by Matthias and Holliday.[2] They took advantage of the hyperfine enhancement of the rf power due to the internal field acting on nuclei in iron. Very soon it was realized—and also used to improve the technique—that the same enhancement mechanism is also responsible for considerable broadening of the NMR lines. In the majority of experiments reported since,[3] a typical linewidth is about 1%. Attempts to minimize the linewidth have been performed,[4] and showed a difficulty in reducing the full width at half maximum below 0.3%. In implanted samples we reported similar linewidths, both with γ and β detection.[5] Hagn *et al.*[6] recently made a great effort to reduce the linewidths in order to resolve quadrupole structure in Ir-Fe and Ni alloys. Already in 1968 Shirley[7] suggested that the hyperfine enhancement—although it eventually permitted a large series of experiments[3] of NMR on oriented nuclei (NMR/ON)—was not a real advan-

tage. If one could use external magnetic fields to orient nuclei, the so-called "brute-force" technique, instead of internal fields in ferromagnets, then the loss of the enhancement factor would be compensated by the narrower linewidth ($\Gamma = 10^3$ Hz instead of 10^6 Hz). Nonmagnetic metals are preferable for magnetic-moment determinations and by using both magnetic and nonmagnetic lattices, hyperfine anomalies as well as Knight-shift determinations would become possible for a whole range of impurity-host combinations. In contrast with a large number of NMR/ON experiments in ferromagnets,[3] only one serious attempt at brute-force NMR (BF/NMR) has been reported: an indication of BF/NMR on Ta^{95}Nb was found by Brewer and Kopp.[8] A study of the line shape was not possible since only one point showed the effect. The difficulties of sample preparation seemed to make the technique rather prohibitive in this case.

The technical requirements of the cryogenic and NMR equipment are also very stringent. The BF/NMR experiments require a homogeneous and stable static magnetic field. A technical description of the equipment used in our experiment will be given elsewhere; we mention only that our 9-T superconducting NbTi solenoid has a homogeneity of 2×10^{-5} over a central sphere of 1 cm diam and a decay rate of 5×10^{-7} T/h at 9 T. The calibration of the magnet was performed by NMR, yielding a magnet constant of 0.106 18 T/A, and regularly checked by performing NMR/ON on Fe^{60}Co. During the experiment the base temperature of our dilution refrigerator was about 7 mK, so that a H/T value of 1300 T/K was available.

For this experiment ^{111}In, with a lifetime of 2.81 d, was chosen (spin $\frac{9}{2}$, g factor 1.23) to give large effects in the available field. Cu was selected as a cubic, diamagnetic host in which In is soluble. The In activity was implanted in a high-purity copper foil up to a dose of 3.33×10^{12} atoms/cm^2 whereafter the foil was mounted in a top-loading cryostat.[9] The maximum source strength was about 10 μCi and the associated radioactive heating was negligible. The anisotropy of the radiation emitted by the oriented nuclei was measured with a Ge(Li) detector. The temperature was determined by monitoring simultaneously the ansiotropy of the 136-keV transition of a Fe^{57}Co thermometer source. Figure 1 shows the observed variation of normalized count rate for the 171- and 247-keV transitions as a function of H/T. The observed anisotropies are in agreement with calculations based on the known g value, decay scheme, and the measured H/T, if a

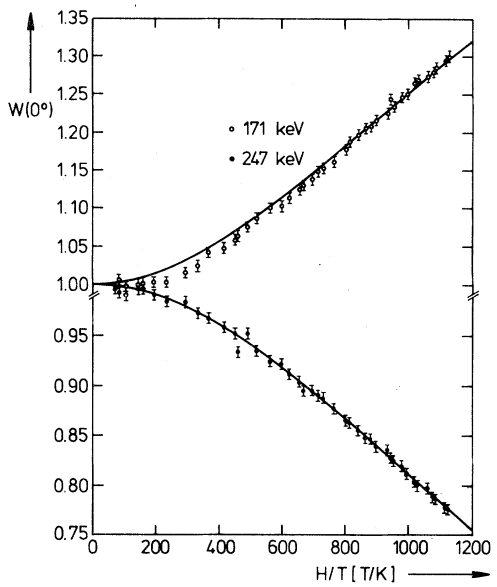

FIG. 1. $Cu^{111}In_{pol}$ anisotropy for the 171-keV (open dots) and the 247-keV (full dots) transitions. The full line indicates the best fit.

constant attenuation factor of 0.90(5) is introduced for all H/T values. This attenuation was also seen in other BF experiments on CuIn.[10,11] An explanation of this attenuation can be found in a supplementary quadrupolar interaction. Indeed perturbed angular correlation and Mössbauer measurements on this system[12,13] indicate that about 10% to 20% of the nuclei experience a large electric field gradient after room-temperature implantation. By supplementary annealing[14] this attenuation can be diminished at the risk, however, of a reduction of the NMR signal.

During the NMR search the polarizing field was kept at 89.998 kG and the intensity recorded in the Ge(Li) detector was used as a resonance indication. The anisotropy was slightly increased by rf heating to approximately + 18% and − 25%, respectively, for the 171- and 247-keV transitions. A resonance search was carried out in the frequency region 84.20–84.70 MHz. Counting periods of 150 s were taken alternately with and without frequency modulation ($\Delta\nu = 20$ kHz at 100-Hz sweeping rate) and separated by $\Delta t = 30$ s to allow for relaxation. Great care was given to stability by regular calibration of the synthesizer (stable to 1 part in 10^7). The added result of ten scans, both downwards and upwards, is shown in Fig. 2. The 171-keV least-squares fitting with a Gaussian-shaped curve, with the experimental modulation width folded in, resulted in $\nu_0 = 84.4240(29)$

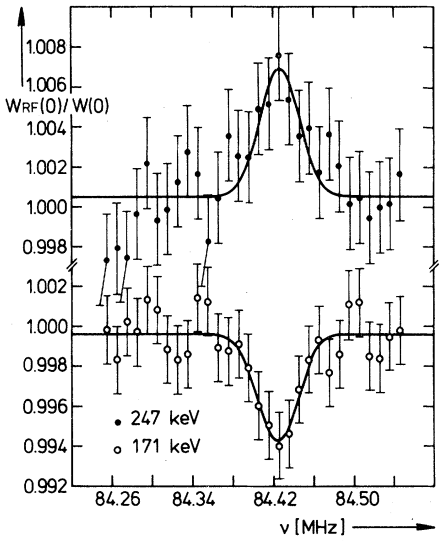

FIG. 2. BF/NMR lines of $Cu^{111}In_{pol}$ for the 171-keV (open dots) and the 247-keV (full dots) transitions.

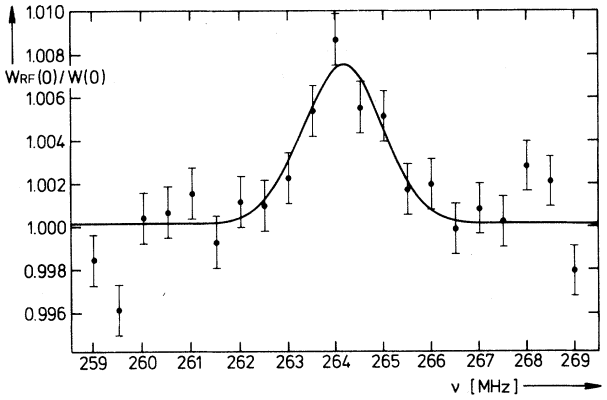

FIG. 3. NMR/ON of $Fe^{111}In_{pol}$ for the 247-keV transition.

MHz (center frequency), $\Gamma = 0.0373(97)$ MHz (full width at half maximum), and $\chi^2 = 10.1$. For the 247-keV transition, the best fit with a χ^2 of 10.9 resulted in a broader line [$\Gamma = 0.084(16)$ MHz]. Therefore the data for the 247-keV transition were fitted with the linewidth obtained from the 171-keV data and resulted in a good fit, $\chi^2 = 13.6$, with $\nu_0 = 84.4246(35)$ MHz. An integrated destruction of anisotropy of the order of 15% was calculated from a maximum amplitude of the effect of about 0.6%.

Sample preparation did not give special difficulties, in contrast with the difficulties encountered by Brewer and Kopp. Also, the NMR search takes on the average no more time than what we are used to when using hyperfine enhancement. Although one can correct the observed linewidth for frequency modulation to give 25.5 kHz,[15] the linewidth remains broader than expected. A broadening of the resonance line by an unstable field was minimized as our magnet proved to have sufficient homogeneity and stability. Although we were far from saturation of the resonance signal, this is again not unusual compared with NMR/ON experiments in ferromagnets. A 100% destruction is seldom reached and is, according to Matthias *et al.*,[16] theoretically not even possible in the case of γ detection. This conclusion is contradicted by Wilson and co-workers[17,18] who predicted that a complete destruction is possible if the rf field is sufficiently large.

In a BF/NMR experiment, the impurity atoms should carry no moments and no hyperfine field should be present. A plot of resonance frequency versus field should then be a straight line through the origin with a slope given by

$$d\nu/dH = (g\mu_N/h)(1+K),$$

where g is the nuclear g factor and K is the Knight shift. In our case the slope is given by 0.93807(5) MHz/T.

Since the magnetic moment of ^{111}In was only known by an atomic-beam measurement as $5.53(6)\mu_N$,[19] we performed a NMR/ON experiment on $Fe^{111}In_{pol}$ in order to enable a determination of the Knight shift. The resonance was found at a frequency of 264.16(8) MHz, yielding a magnetic moment of $5.497(6)\mu_N$ corrected for the polarizing field. The resonance is displayed in Fig. 3. The magnetic-moment value can be corrected for the Knight shift in Fe [$-2.4(6)\%$][20] to give $5.499(7)\mu_N$. In Ref. 20 it is also shown that quadrupolar corrections can be disregarded. Furthermore, an experiment was performed by Hagn and Zech[21] who obtained a value of $5.504(10)\mu_N$, confirming our value. Combining these results we obtain a magnetic moment of $5.502(6)\mu_N$. A comparison of g factors obtained from different experiments is made in Table I.

From Table I one can determine the Knight shift of In in Cu as 0.65(11)%. Since we work at very low concentration, the resultant Knight shift is ideally suited for comparison with theory. The redistribution of conduction electrons which accompanies the solution of a foreign atom has been mostly studied by classical NMR through measurements on the solvent: only in a few cases are results available on the solute. Even in these measurements, however, the solute shift at "in-

TABLE I. Comparison of g factors of ^{111}In from different methods.

$g(^{111}\mathrm{In})$	Value	Method	Reference
$g(^{111}\mathrm{In})$	1.2200(133)	ABMR [a]	Marino, in Ref. 19 [a]
$g(^{111}\mathrm{In})$	1.2227(13)	NMR/ON in Fe	This work and Ref. 21
$g(^{111}\mathrm{In})(1+K)$	1.2306(1)	BF/NMR in Cu	This work

[a]Atomic-beam magnetic resonance; L. L. Marino, UCRL Report No. UCRL-8721, 1959 (unpublished).

finite" dilution has usually been obtained by extrapolation from several-percent alloys. Moreover, the linewidth[22] as well as the magnitude of the Knight shift itself[23] can vary with concentration. Our value of 0.65(11)% is nevertheless in excellent agreement with the value of 0.58(2)% from Ref. 23, indicating that at least in this case the Knight shift is not very dependent on concentration. The theoretical importance of calculating the contact interaction of an impurity, its internal field, and the relation to the energy bounds of the solvent have been discussed at length by Bennett, Mebs, and Watson.[24] More recent calculations[25] claim an *"ab initio"* approach with, so far, an impressive agreement with experiment. Calculations are in progress for the case In(Cu). Clearly more experiments in the very low concentration region would be helpful, especially in noble metals.

In summary, we have merely shown the feasibility of nuclear magnetic resonance on nuclei oriented by the brute-force method. The observed resonance lines are, however, somewhat broader than expected, and a rather small resonant anisotropy destruction has been obtained; work is still needed to reach the theoretical linewidth. On the other hand, this result demonstrates that once all rather demanding experimental requirements are satisfied, the NMR on oriented nuclei is equally easy with use of external fields, compared with the commonly used hyperfine enhancement. The use of external fields combined with NMR allows low-temperature nuclear orientation (NO) to break free from the restriction to ferromagnets without the discussions about attenuation factors that plague integral BF/NO experiments.[26] Finally, the accuracy becomes comparable to what one expects in a normal NMR measurement. BF/NMR creates the possibility of measuring a series of hyperfine parameters for a new range of impurity-host combinations because the use of implanted radioactive nuclei lifts the restriction to alloys or soluble elements.

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