# Hyperfine Interaction of Xenon in Iron

E. Schoeters, R. Coussement, R. Geerts, J. Odeurs, H. Pattyn, R. E. Silverans,* and L. Vanneste
*Instituut voor Kern- en Stralingsfysika, Leuven University, 3030 Heverlee, Belgium*
(Received 27 April 1976)

The hyperfine interaction of xenon atoms ($^{129m}$Xe) implanted in iron has been studied with nuclear magnetic resonance on oriented nuclei. A sharp resonance line was found at $\nu_1 = 188.12 \pm 0.02$ MHz for substitutionally implanted atoms. In addition a broad resonance line corresponding to vacancy-associated xenon atoms was detected at $\nu_2 = 152.0 \pm 0.6$ MHz. By measuring $\nu_1$ for different external fields, the nuclear $g$ factor of the $I^\pi = \frac{11}{2}^-$ state ($g = 0.154 \pm 0.005$), as well as the values and the sign of the internal fields, was determined.

The major advantage of the technique of nuclear magnetic resonance on oriented nuclei (NMR/ON) for studying hyperfine interactions (HI) resides in the fact that it combines the resolution of the classical NMR technique with the sensitivity of the methods using radiative detection. The fact that nuclear orientation is normally performed using the large hyperfine field in a ferromagnetic lattice leads, however, to an inhomogeneous broadening of the NMR lines which normally keeps one from studying field distributions and linewidths. We present a NMR/ON experiment from which, for the first time, meaningful information has been obtained about different field sites of the same implanted atom through the measurement of their NMR lines and the linewidths that correspond to them.

This study was performed on what is considered the "prototype" of HI experiments, xenon implanted in iron: It has been studied intensively since 1967 in nuclear orientation (NO), perturbed angular correlation (PAC), Mössbauer, and channeling experiments.[1-8] A more or less chronological but incomplete review can be found in Refs. 1–8. This review proves that these methods provide valuable and complementary information, but it also demonstrates their limitations. Channeling does not measure the HI itself and cannot distinguish inequivalent substitutional positions; NO and PAC are integral techniques giving only average values; and Mössbauer data suffer from the appearance of many correlated parameters and the fact that the different components are not sufficiently resolved. Therefore we planned a NMR/ON experiment on $^{129m}$Xe in iron, in order to get more accurate and unambiguous information about the hyperfine interaction and the corresponding location in the lattice. $^{129m}$Xe was obtained by double-neutron capture on KI at the BR2 reactor, Mol, Belgium, since irradiation of xenon gas could not give large enough activities for this experiment. The activity was implanted into polycrystalline iron at room temperature with an accelerating voltage of 75 kV with the isotope separator at the Instituut voor Kern- en Stralingsfysika. No further heat treatment was done. The final dose was $10^{14}$ ions/cm$^2$ corresponding to a concentration of 0.5 at.% (calculation based on the Lindhard-Scharff-Schiøtt theory[9]). As it was shown previously[8,10] that the site populations are dose dependent, the concentration was chosen in such a way that a reasonable occupation of the two highest field positions could be expected. The isomeric $I^\pi = \frac{11}{2}^-$ ($T_{1/2} = 8.0$ d) state decays by an $M4$ radiation of 196 keV. The large anisotropy of this transition was detected with two 3-in.×3-in. NaI crystals, positioned at 0° and 90° with respect to the field direction established by the polarizing magnet. Essential for the success of this experiment was the possibility of accumulating statistics during relatively long periods of time. This is because of the normal smallness of the NMR destruction, the large conversion of the $M4$ transition, and the fact that (as we knew from Mössbauer experiments) sometimes only a small fraction of nuclei are at one particular field site. Therefore a high power $^3$He-$^4$He dilution refrigerator was used that allowed us to cool sources of several hundred microcuries down to 18 mK.

Two high-field components have been extracted from the Mössbauer data, a first one $B_1 \simeq 1500$ kG and a second one $B_2 \simeq 1200$ kG. With a magnetic moment[11] $|\mu| = (0.80 \pm 0.10)\mu_N$ a first resonance was looked for in the region from 140 to 190 MHz. A sharp resonance line was found at $\nu_1 = 188.20 \pm 0.02$ MHz with a linewidth [full width at half-maximum (FWHM)] of only $440 \pm 30$ kHz in a polarizing field of 0.8 kOe. A modulation amplitude $\Delta\nu = \pm 100$ kHz has been used. In a second series of scans, high statistical accuracy brought

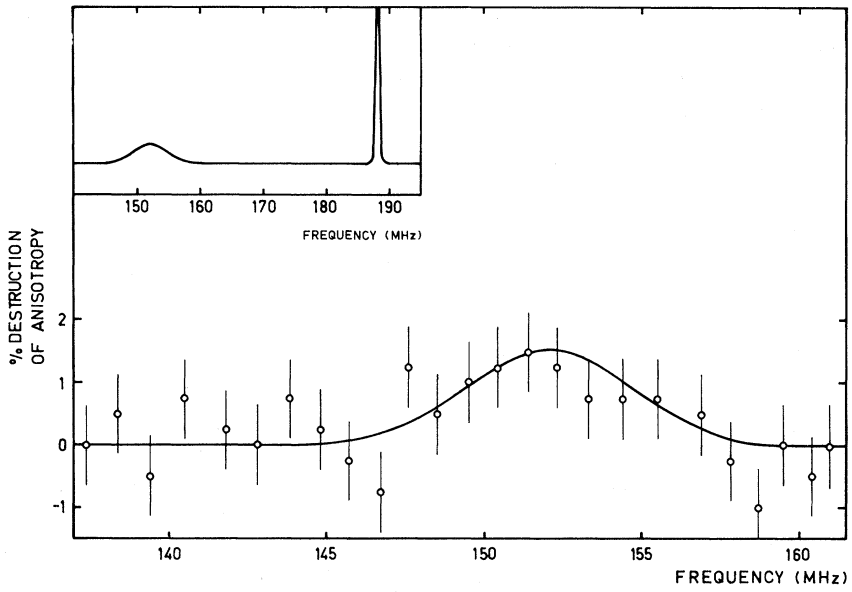


FIG. 1. Resonance curve corresponding to the $B_2$ site. In the inset both resonance lines are displayed together. Here the vertical scale is arbitrary.

out a second resonance at $\nu_2 = 152.0 \pm 0.6$ MHz with a FWHM of $6.2 \pm 1.6$ MHz. The effect was established by comparing, during several weeks, 5-min spectra with FM on ($\Delta\nu = \pm 1$ MHz) and FM off, in order to eliminate the effect of cw heating. Between those counts 1 min was left for the nuclei to relax (the relaxation time is, according to experimental estimates, of the order of 10 sec). No other resonance could be detected up to now in the region from 120 to 200 MHz, and by repeated scans any error other than statistical could safely be ruled out. The second resonance effect is much reduced compared to the major one because of the smaller anisotropy, the broadening of the line, and the smaller fraction of participating nuclei (probably a 3 times smaller fraction). Both resonance lines are displayed in the inset of Fig. 1 to give an idea of their relative widths and the resolution obtained with the NMR/ON technique. An example of an actual scan through $B_2$ and $B_1$ is shown respectively in Figs. 1 and 2(a). In order to reduce the rather large uncertainty on the $g$ factor of the $\frac{11}{2}^-$ state and to get information independent of other techniques, we measured the resonance frequencies $\nu_1$ for different external fields [Fig. 2(b)]. Because of the very high internal field of xenon in iron, large external field variations are required to produce resonable fre-

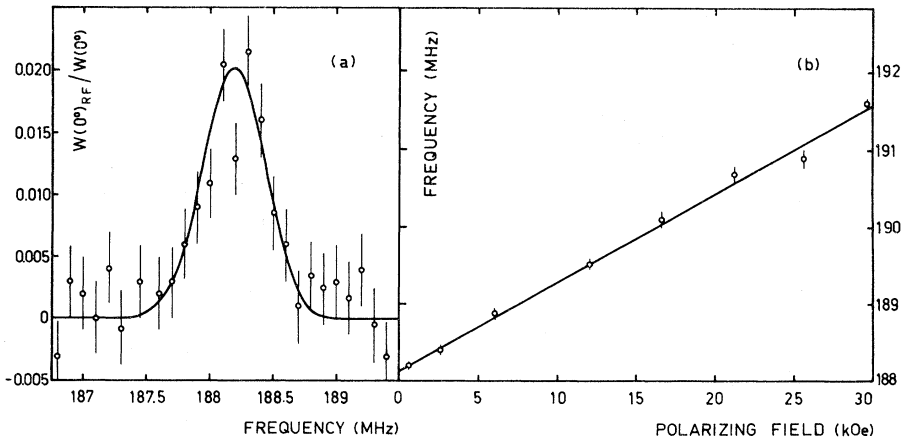


FIG. 2. (a) A typical example of a $B_1$ resonance line for a polarizing field of 0.65 kOe. (b) The field dependence of the resonance frequency.

quency shifts. We measured the resonance up to 30 kOe with a superconducting magnet. There is a strong reduction of the NMR signal at high fields due to the loss in hyperfine enhancement. In this way we obtained $|g_{11/2}| = (0.154 \pm 0.005)\mu_N$ or $|\mu_{11/2}| = (0.85 \pm 0.03)\mu_N$, $B_1 = +1603 \pm 52$ kG, and $B_2 = 1295 \pm 45$ kG (both corrected for the applied field). The ratio of the two fields could be determined much more accurately: $B_2/B_1 = 0.808 \pm 0.003$. This value agrees perfectly with the one predicted by de Waard *et al.*[6] by taking squares of overlap-integral sum ratios, thus giving strong evidence for the proposed origin of those hyperfine fields. The shift towards higher frequencies experimentally confirms the positive sign of the field, in agreement with the theoretical expectations.

By increasing the rf power over a large range, we achieved a saturated anisotropy destruction of 55%. However, in the presence of more than one hyperfine-interaction component contributing to the anisotropy, this does not mean a minimum of 55% of the Xe nuclei being in a $B_1$ site. In this case the anisotropy is given by the formula

$$\epsilon(\theta, T) = \sum_{i=1}^{n} \alpha_i \epsilon_i(\theta, T), \qquad (1)$$

where $\alpha_i$ is the fractional occupation of site $i$ ($\sum_{i=1}^{n} \alpha_i = 1$), $\epsilon_i(\theta, T)$ is the corresponding anisotropy, and $n$ equals the number of different sites. One has[12]

$$\epsilon_i(\theta, T) = \sum_{k=2,4} U_k F_k B_k(i) P_k(\theta),$$

where the $U_k$ and $F_k$ are radiation parameters, the $B_k$ describe the degree of orientation, and the $P_k$ are Legendre polynomials containing the angular dependence of the anisotropy. Hence it appears that $\alpha_1^{(\min)} = \{\epsilon(T) - \epsilon^{rf}(T)\}/\epsilon_1(T)$. In this equation $\epsilon(T)$ represents the observed anisotropy, $\epsilon^{rf}(T)$ the residual anisotropy at resonance, and $\epsilon_1(T)$ is not the observed anisotropy but the anisotropy calculated if a 100% substitutional hyperfine interaction is present. Such a calculation gives us $\alpha_1^{(\min)} = 0.34 \pm 0.05$.

After the NMR/ON measurement, a separate run was done for a conventional NO experiment. The anisotropy of the radiation emitted by the oriented nuclei was measured with two Ge(Li) detectors at 0° and 90° with respect to the applied field. The temperature was determined by monitoring simultaneously the anisotropy of the 136-keV transition in a $^{57}$Co(Fe) sample. The anisotropies observed for $^{129m}$Xe were analyzed using a two-site model, one corresponding to the $B_1$ field and one corresponding to zero field. By introducing the hyperfine splitting constant as determined in the NMR experiment, we could perform a one-parameter least-squares fit for the substitutional fraction. This procedure yielded $\alpha_1^{(\max)} = 0.52 \pm 0.01$, but it only constitutes an upper limit. It was not possible to determine simultaneously $\alpha_1$ and $\alpha_2$ ($B_2$ fraction) by performing a two-parameter fit to the NO data. However, in a three-site model [$n = 3$ in Eq. (1)] with field values $B_1 = 1603$, $B_2 = 1295$, and $B_3 = 0$ kG, we can correlate $\alpha_1$ and $\alpha_2$ ($\alpha_3 = 1 - \alpha_1 - \alpha_2$) by fitting $\alpha_1$ for different values of $\alpha_2$. In this way we obtained a relation $\alpha_1 = 0.52 - 0.78\alpha_2$. If the value $\alpha_1^{(\max)}$ derived from the NMR experiment would really correspond to complete destruction of the associated anisotropy and hence constitute the real $B_1$ fraction, this relationship would imply a value $\alpha_2^{(\max)} = 0.23 \pm 0.06$. As 100% destruction has never been reported, we add the superscript (max) to it. In practice a destruction of about 80% often seems to be a limiting value. Such an assumption would imply $\alpha_1 = 0.40 \pm 0.05$ and $\alpha_2 = 0.15 \pm 0.05$, in good agreement with the relative intensities of both NMR lines when taken at the same power level, and with the data resulting from Mössbauer experiments.

Another remarkable result of this experiment is the sharpness of the major resonance line (FWHM = 440 kHz). This is the narrowest linewidth observed up to now for a polycrystalline sample, and it is comparable to the best results obtained with sources prepared by diffusion into single crystals. This effect might be an indication for a supplementary source of information, unexplored so far, as it may reflect the inertness of the xenon atomic core to polarizing effects. It also contradicts the widespread opinion that implanted sources should inherently show large inhomogeneous broadening due to radiation damage. In this way the broadening of the second line may be relevant for the magnitude of the quadrupole interaction seen by the Xe nuclei in a $B_2$ site. A simple calculation of the lattice contribution to the electric field gradient due to the first-near-neighbor vacancy—making use of the lattice parameters given by Drentje and Ekster[13]—gives $V_{zz} = 4.5 \times 10^{20}$ V/m$^2$. If we take[14] $Q_{11/2} = 1.3 \times 10^{-28}$ m$^2$ we get an estimate of the quadrupole coupling constant of at least (neglecting the Sternheimer antishielding factor)

$$P = 3eQV_{zz}/h4I(2I - 1) = 0.15 \text{ MHz}$$

and the resonance will accordingly be split into $2I = 11$ components separated in frequency by $\Delta\nu$

$= 2P(\frac{3}{2}\cos^2\varphi - \frac{1}{2})$. Here $\varphi$ is the angle between the magnetic interaction axis and the symmetry axis of the electric quadrupole interaction. This gives rise to a distribution of resonance frequencies which has the right order of magnitude when compared to the experimental broadening. In that case the $B_2$ and $B_2/B_1$ values should also be corrected for a shift of the central frequency. A purely magnetic broadening, as well as other explanations, cannot be ruled out. Yet, as we have for the first time the opportunity to study an isolated impurity-vacancy system, it would be very valuable to do more detailed experiments. In this respect it would be highly desirable to repeat these measurements on single crystals: By varying the angle $\varphi$ one could eventually learn more about the origin of the broadening.

The authors with to thank the Belgian Interuniversitair Instituut voor Kernwetenschappen for financial support.

*Aangesteld navorser National Fonds voor Wetenschappelijk Onderzoek.

[1]L. Niesen, J. Lubbers, H. Postma, H. de Waard, and S. A. Drentje, Phys. Lett. B24, 144 (1967).
[2]H. de Waard and S. A. Drentje, Proc. Roy. Soc. London, Ser. A 311, 139 (1969).
[3]L. C. Feldman and D. E. Murnick, Phys. Rev. B 5, 1 (1972).
[4]H. Pattyn, R. Coussement, G. Dumont, E. Schoeters, R. E. Silverans, and L. Vanneste, Phys. Lett. A45, 131 (1973).
[5]M. Van Rossum, G. Langouche, H. Pattyn, G. Dumont, J. Odeurs, A. Meykens, P. Boolchand, and R. Coussement, J. Phys. (Paris), Colloq. 35, C6-301 (1974).
[6]H. de Waard, R. L. Cohen, S. R. Reintsema, and S. A. Drentje, Phys. Rev. B 10, 3760 (1974).
[7]S. R. Reintsema, S. A. Drentje, P. Schurer, and H. de Waard, Radiat. Eff. 24, 145 (1975).
[8]D. M. Gordon, L. Eytal, H. de Waard, and D. E. Murnick, Phys. Rev. C 12, 628 (1975).
[9]J. Lindhard, M. Scharff, and M. E. Schiøtt, K. Dan. Vidensk. Selsk., Mat.-Fys. Medd. 33, 14 (1963).
[10]J. Odeurs, R. Coussement, G. Dumont, H, Pattyn, E. Schoeters, R. E. Silverans, and L. Vanneste, to be published.
[11]R. E. Silverans, R. Coussement, H. Pattyn, E. Schoeters, and L. Vanneste, Z. Phys. 267, 145 (1974).
[12]R. J. Blin-Stoyle and M. A. Grace, in *Handbuch der Physik*, edited by S. Flügge (Springer, Berlin, 1957), Vol. 42, p. 555.
[13]S. A. Drentje and J. Ekster, J. Appl. Phys. 45, 3242 (1974).
[14]L. S. Kisslinger and R. A. Sorensen, Rev. Mod. Phys. 35, 853 (1964).

# Observation of Surface Excitons in Rare-Gas Solids*

V. Saile, M. Skibowski,† and W. Steinmann
*Sektion Physik der Universität München, 8000 München 40, Federal Republic of Germany*

and

P. Gürtler
*II. Physikalische Institut der Universität Hamburg, 2000 Hamburg 50, Federal Republic of Germany*

and

E. E. Koch and A. Kozevnikov‡
*Deutsches Elektronen-Synchrotron DESY, 2000 Hamburg 52, Federal Republic of Germany*
(Received 22 April 1976)

Evidence is obtained for the excitation of surface excitons in solid Ar, Kr, and Xe in optical transmission and reflection experiments using synchrotron radiation. They are located at photon energies ranging from 0.6 eV for Ar to 0.1 eV for Xe below the corresponding bulk excitons excited from the valence bands. Their halfwidths (20–50 MeV) are less than half the values found for the bulk excitons. Some are split by an amount considerably smaller than the spin-orbit splitting of the valence bands.

In this Letter we report the first evidence for surface excitons in rare-gas solids. They are located at photon energies close to the corresponding bulk valence excitons. We consider them to represent new electronic states which are introduced by the presence of the surface and are spatially confined to a region close to it. They are different from electromagnetic surface