in Molecules and Ions, edited by L. E. Sutton (Chemical Society, London, 1965).

[19]H. Micklitz and P. H. Barrett, Phys. Rev. Letters 28, 1547 (1972).

[20]T. K. McNab, H. Micklitz, and P. H. Barrett, Phys. Rev. B 4, 3787 (1971).

PHYSICAL REVIEW B VOLUME 7, NUMBER 3 1 FEBRUARY 1973

Lattice-Location Study of Hf Implanted in Ni

E. N. Kaufmann, J. M. Poate, and W. M. Augustyniak
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 31 August 1972)

The channeling technique has been used to study the lattice location of Hf implanted in single-crystal Ni samples. Results indicate that about one-half the Hf atoms occupy regular Ni lattice sites, the remainder being in some form of precipitate. It was found that annealing the sample above 600 °C promotes further precipitation of the impurity. These results are compared with recent hyperfine-interaction experiments on the same system.

I. INTRODUCTION

The hyperfine magnetic fields at dilute impurities in ferromagnetic-host matrices have been widely studied using such techniques as Mössbauer-effect spectroscopy and perturbed-angular correlations. In some cases where multiple fields have been observed or discrepancies have arisen among various measurements, the additional information provided by impurity-lattice-site-location measurements, using the channeling technique, has served to clarify the interpretation of results by better defining the nature of the system under study and its dependence on sample preparation techniques.[1,2] We have applied the channeling technique to the study of the *Ni* Hf system in order to better understand the origin of wide variations in reported results of perturbed-angular-correlation measurements on sources of ^{181}Hf nuclei imbedded in Ni. Whereas in all cases[3–8] the same value of the magnetic-hyperfine field (at the ^{181}Ta daughter nucleus) of $H_{\mathrm{hf}} \simeq -90$ kOe has been seen, reports concerning the fraction of nuclei experiencing this field and the presence of additional interactions are in disagreement.

A survey of the reports in question leads us to surmise that the origin of the discrepancies lies in the different source-preparation techniques employed. Three methods of alloying the ^{181}Hf impurity with Ni have been employed; melting,[3,6,8] diffusion,[7] and isotope-separator ion implantation.[4–6] In some instances high-temperature ($\geqslant 600$ °C) annealing was performed after the introduction of the Hf.[3,8] Because the channeling technique must utilize single-crystal hosts it does not readily lend itself to the study of dilute impurities introduced in the melt.[9] A heavy implanted impurity in a light host at concentrations of the order of 1 at.%, however, is ideally suited to a channeling study which employs Rutherford-backscattered ions.[1,2,10] In Sec. II the details of sample preparation and experimental technique are described. Section III presents the results for samples before and after annealing at various temperatures. In Sec. IV the individual perturbed-angular-correlation experimental results are reviewed and interpreted in terms of our observations.

II. EXPERIMENTAL DETAILS

A Ni single crystal of high purity obtained from Semielements Corp. was oriented and cut to the shape of a disc 1 cm in diam and 1 mm thick so that the ⟨110⟩ crystallographic direction was normal to the plane of the disc. The sample was Syton polished to remove damage from the surface as verified by Laue x-ray-diffraction photographs. An isotope separator operated at 150 kV was employed to implant singly ionized ^{180}Hf ions to a dose of 2×10^{14} cm^{-2}. The implant was carried out at room temperature with the sample oriented such that the implanted ions entered in a nonchanneling, i.e., random, direction. The calculated projected range of the implanted ions[11] is ~ 200 Å with an associated range straggling of ± 60 Å which, for the stated dose, implies a local volume concentration of Hf in Ni of 0.2 at.% in the implanted layer. This concentration would correspond to 10 μCi of ^{181}Hf activity implanted over an area of 0.01 cm^2 and is thus comparable to concentrations used in the radioactivity experiments.

The sample was mounted on a two-axis goniometer and placed in the beam line of a 2-MV Van de Graaff accelerator. In some instances a heating goniometer capable of generating a 700 °C sample temperature was used. Beams of 1.8- to 2.0-MeV ^{4}He$^+$, ^{12}C$^+$, and ^{14}N$^+$ were used at various times for the channeling measurements. The ion-beam angular divergence was defined to better than 0.05° by suitable collimation. Elastically backscattered ions from the sample target were detected in a 50-mm^2 annular Si surface-barrier detector. The detector showed ~ 16-keV energy resolution for He ions and about 40 keV for the heavier ions.

Backscattered-ion energy spectra were stored in a PDP-8 computer coupled to an analog-to-digital converter. Several spectra corresponding to ions incident parallel to various crystal axial channels, as well as in random directions, were accumulated. During each accumulation the integrated incident-beam current on the target was measured. This process was repeated after each 30-min annealing of the sample at the sequence of temperatures; 150, 250, 350, 450, 550, and 650 °C. In each case the yield of ions backscattered from the Hf-impurity layer and the Ni host were separately determined from the spectra, where the difference in kinematic energy loss permits identification of the heavy impurity and lighter host.

Because of "flux-peaking" effects in channeling,[12,13] angular scans of the host and impurity are necessary for identification of the impurity location within the host lattice. A substitutional impurity will give rise to exactly the same angular behavior as the host.[12] An interstitial impurity however will not display this angular dependence but may even give rise to a peak in scattering yield in an aligned direction, as has been seen for interstitial impurities in the *Si*Yb and *W*B systems.[14,15] In the present study of *Ni*Hf, detailed angular scans of the unannealed sample were performed by measuring the scattering yields from host and impurity as a function of incident-beam entrance angle to each of various axial channels. These angular scans covered the range from precise alignment with the axis to misalignment by approximately twice the critical angle for channeling.[16] Some care was taken to avoid a beam direction for which planar channeling occurs in the axially misaligned cases.

III. RESULTS

The energy spectra of Fig. 1 taken for 2.0-MeV $^{12}C^+$ ions incident in a ⟨110⟩ channeling direction and a random direction are typical of the data collected. Indicated in the figure are the regions over which the impurity peak was summed and the point in the host continuum at which the ratio (χ_{min}) of the channeled-to-random yield was computed. Backgrounds, arising principally from electronic-pulse pile-up effects in the amplifier system, were subtracted from the Hf yields. At worst the backgrounds only constituted 10% of the total yield.

The yields as a function of angle for 2.0-MeV $^{14}N^+$ ions for the unannealed case are shown in Fig. 2, where the host and impurity yields have each been normalized to unity near the extremes of the angular ranges. It is immediately seen that in each case the reduction in scattering yield of the impurity is only 50% of the reduction seen in the host and that the shapes of host and impurity profiles are the same with the same critical angles for channeling. This is a very strong indication that 50% of the Hf impurity atoms occupy regular Ni lattice sites, but that the remainder of the impurity appears to have no specific crystallographic-site preference, as would be the case for impurity clusters or a second-phase precipitate, for example.

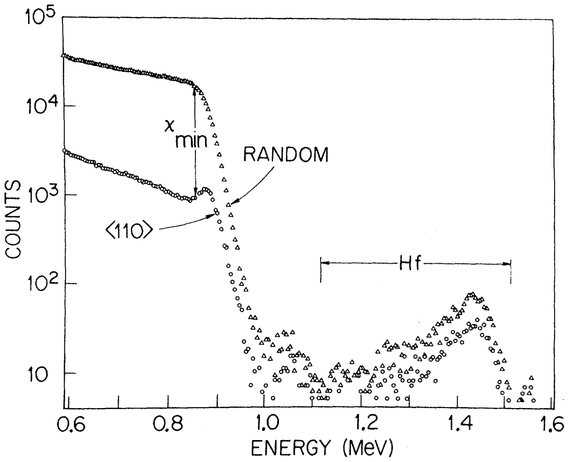

FIG. 1. Backscattered-ion energy spectra for 2.0-MeV $^{12}C^+$ ions, for the same integrated charge, incident in ⟨110⟩ and random directions on a Ni single crystal implanted with 2×10^{14} cm^{-2} ^{180}Hf ions at an energy of 150 keV. The 50% reduction in the Hf yield for the channeling direction is evident. The small peak at the high-energy end of the spectrum correlates well with a very low level ~ 10^{13} atoms/cm^2 of heavy-metal impurity such as Au on the surface of the Ni. (The expected backscattered energy from Au is 1.57 MeV.)

Whereas angular scans were carried out on the sample prior to annealing, single measurements were made on and off axis after each annealing period. The impurity yields for channeled (Y_C) and random (Y_R) incidence are combined with the host minimum yield (χ_{min}) to find the substitutional fraction $S=(1-Y_C/Y_R)/(1-\chi_{min})$, which has been tabulated for all cases studied in Table I. Except for the result at the highest annealing temperature, the Hf shows approximately 50% substitutionality in Ni. This nomenclature and definition of substitutional fraction can lead to ambiguities in interpretation if used without recourse to knowledge of the detailed angular scans. However, the angular-scan measurements taken prior to annealing indicate the absence of such complicating factors as flux-peaking effects. This definition of S therefore does indicate the relative number of atoms on regular lattice sites.

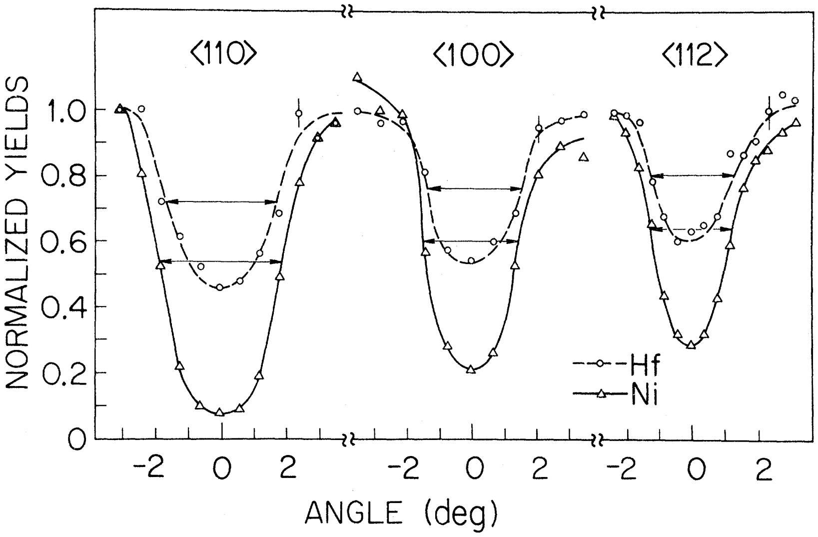

FIG. 2. ⟨110⟩, ⟨100⟩, and ⟨112⟩ angular scans for 2.0-MeV $^{14}N^{+}$ ions for the unannealed case. The host and impurity yields have been normalized to unity at the ends of the scans where the yields are equal to that for a random direction. The smooth curves through the host and impurity scans have been drawn to guide the eye. The horizontal lines indicate the critical angles $2\psi_c$ for each scan. The ratio of the critical angles for the three axes agrees well with channeling theory (Ref. 16).

It is unlikely that the nonsubstitutional fraction arises from lattice damage from the implant or the probing beam since no change in S is observed after damage has been annealed (as indicated by the decreases in χ_{min} at 150 and 450 °C in Table I). If a substantial fraction of the nonsubstitutional Hf atoms were, in fact, in regular interstitial sites, then this would have been revealed in the axial scans. The most likely interstitial site would be the body center, or octahedral position, which appears fully substitutional along the ⟨100⟩ direction but interstitial in the ⟨110⟩ direction. However, the ⟨100⟩ and ⟨110⟩ angular scans indicate the same substitutionality, thus ruling out the octahedral site. The fact that the ⟨112⟩ angular scan also displays the same substitutional behavior would also appear to rule out any other regular interstitial site.

The spectra shown in Fig. 3 demonstrate that the abrupt decrease in S to ~ 10%, after annealing at 650 °C, was accompanied by a migration of the Hf impurity toward the surface of the Ni crystal. The depth resolution of the 2.0-MeV $^{12}C^{+}$ probe, calculated from the experimental energy resolution and stopping power for C in Ni,[17] is 80 Å. It can be seen that the Hf impurity migrates 200 Å, in good agreement with the projected range of the implanted Hf in Ni. The energy of ions backscattered from Hf at the surface was obtained by calibrating the system against a Hf-metal sample. Although some fraction of the Hf impurity following the 650 °C anneal must be in an oxide layer, the width of the impurity peak in the spectra indicates that the Hf extends some 100 Å (at least) into the Ni beyond the 15- to 20-Å thick oxide layer.[18] Thus, the drastic reduction in substitutional fraction cannot be assigned entirely to impurity in the oxide, and it

TABLE I. Compilation of the substitutional fraction S and host minimum yield χ_{min} as a function of annealing temperature. The errors in S and χ_{min} are the order of 5%.

		⟨110⟩		⟨112⟩		⟨100⟩	
Temperature	Beam	χ_{min}	S	χ_{min}	S	χ_{min}	S
20 °C	2.0-MeV $^{14}N^{+}$	0.08	0.59	0.29	0.54	0.21	0.57
	2.0-MeV $^{4}He^{+}$	0.07	0.54				
150 °C	1.8-MeV $^{12}C^{+}$	0.04	0.53	0.11	0.63		
250 °C	2.0-MeV $^{12}C^{+}$	0.04	0.54	0.12	0.48		
350 °C	2.0-MeV $^{12}C^{+}$	0.04	0.43				
450 °C	2.0-MeV $^{12}C^{+}$	0.03	0.43				
550 °C	2.0-MeV $^{12}C^{+}$	0.03	0.45				
650 °C	2.0-MeV $^{12}C^{+}$	0.03	0.13	0.07	0.07		

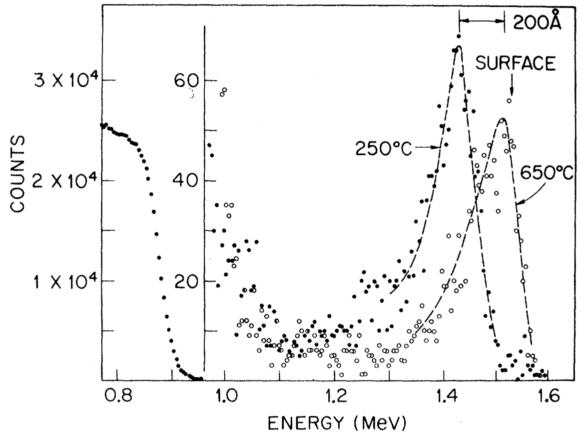

FIG. 3. Backscattered energy spectra for 2.0-MeV $^{12}C^{+}$ ions for the 250 and 650 °C anneal with the beam incident in a random direction. Only one of the two identical host spectra has been plotted. In the high-energy range, the vertical scale has been changed. The migration of Hf toward the surface at temperatures above 650 °C is evident.

must be concluded that at temperatures at or above ~ 600 °C the Hf segregates or precipitates out of the Ni lattice. This is consistent with metallurgical studies[19] which show that a very dilute Hf impurity (< 0.1 at.%) in Ni increases the material hardness and raises the recrystallization temperature of cold-worked samples, presumably by precipitation hardening.[20]

IV. COMPARISON WITH PERTURBED-ANGULAR-CORRELATION MEASUREMENTS

The perturbed-angular-correlation measurements on the $Ni\,^{181}$Hf system have all been of the time-differential type in which the anisotropy of the γ-ray correlation through a long-lived ($T_{1/2} \approx 10$ nsec) state in the daughter nucleus ^{181}Ta is observed as a function of the time spent in that state. The frequency of oscillations in the anisotropy yields the magnetic-hyperfine-interaction strength, i.e., the nuclear-Larmor-precession frequency ω_L. The amplitude assigned to those oscillations, when compared with the full amplitude theoretically available from the γ-γ cascade, yields the fraction of nuclei precessing at the frequency ω_L.

All measurements to date have observed a frequency corresponding to a hyperfine field of $H_{\text{hf}} \approx -90$ kOe. The largest amplitude observed corresponded to a source prepared by single-crystal growth from the melt[6] for which about 85% of the impurity resided at the unique field site. Sources prepared by quenching from the melt[8] also yielded large fractions of the order of 60 to 80% but displayed a second group of nuclei which experienced a small positive field. Annealing of the sample at 800 °C for 4 h resulted in a substantial decrease in the high-field fraction and a disappearance of the low field. A sample[3] formed by melting, but annealed at 950 °C for 4 h before the measurement, showed only 4% of the impurity at the unique field site. The annealing process clearly drives a large fraction of the impurity atoms to low- or zero-field environments such as clusters or precipitates or into grain boundaries and is consistent with our observation of impurity motion and reduction in S at the highest annealing temperature. Annealing also heals defects frozen in by quenching from high temperature which can account for the disappearance of the low positive field shown in Ref. 8. The improved values of $\chi_{\min}$ (see Table I) verified that Ni lattice damage will anneal well below temperatures employed in the above experiments.

In those cases where isotope-separator implantation was used, fractions of nuclei at the unique field site ranged from ~ 30%[5] to 70%[4] with most of the remaining fraction apparently seeing no field. In some instances the presence of additional interactions have been suspected, usually because the high-field and zero-field fractions did not sum to 100% or because of weak additional frequencies visible in the Fourier-transformed data.[21] The lattice-location results of the Sec. III are in qualitative agreement with implanted-source observations, in that about 50% of the impurity occupies regular lattice sites where the unique -90-kOe field presumably acts, and the remainder sits in clusters or precipitates of some kind. The channeling measurement also indicates the presence of lattice defects created by implantation which are probably responsible for the observation of the additional interactions mentioned above.

V. SUMMARY

We can conclude that, although the maximum solid solubility of Hf in Ni is 0.7 at.%[18] at elevated temperatures (~ 1200 °C), the solubility at room temperature is very small. Thus in order to retain a sufficient amount of impurity at room temperature the alloy must be in a nonequilibrium supersaturated state. This state can be achieved by either quenching from the melt or implantation. The quenching process also freezes in lattice defects but appears to give the larger substitutional fraction, whereas implantation gives a somewhat smaller fraction on regular lattice sites and also introduces lattice damage artificially in the vicinity of the impurity. In any case, attempts to anneal the alloy promote precipitation of the Hf and allow the Hf to migrate to nonmagnetic sites and perhaps into grain boundaries. The above comparison of hyperfine field and lattice-location measurements clearly indicates that the field of $H_{\text{hf}} \approx -90$ kOe is to be associated with Ta at a regular Ni lattice site.

The channeling measurements themselves are of interest in that they reveal unambiguously a mixed site for room-temperature implants of Hf and Ni. Some 50% of the Hf atoms are in true substitutional positions. The remaining 50% are randomly distributed but are not correlated with the lattice damage caused by the implantation. It is most likely that this random fraction is due to Hf which has precipitated out of the lattice. This phenomenon of approximate equipartition between a substitutional and random site has also recently been observed for the cases of Xe and Yb implanted in Fe.[22,23] As in the present work, the substitutional fraction disappears under suitable annealing conditions.

ACKNOWLEDGMENTS

The authors are indebted to W. F. Flood for his expert crystal preparation and J. W. Rodgers for performing the ion implantation. We also appreciate helpful discussions with Dr. F. C. Zawislak, Dr. J. D. Rogers, and Dr. J. A. Golczewski.

[1] L. C. Feldman and D. E. Murnick, Phys. Rev. B **5**, 1 (1972).

[2] L. C. Feldman, E. N. Kaufmann, D. W. Mingay, and W. M. Augustyniak, Phys. Rev. Lett. **27**, 1145 (1971).

[3] J. C. Vanderleeden, in *Hyperfine Structure and Nuclear Radiations*, edited by E. Matthias and D. A. Shirley (North-Holland, Amsterdam, 1968), p. 495.

[4] N. Buttler, thesis (University of Bonn, 1970) (unpublished).

[5] J. A. Cameron, P. R. Gardner, W. V. Prestwich, and Z. Zamori, Can. J. Phys. **48**, 2725 (1970); and J. S. Barrett, J. A. Cameron, Z. Zamori, and D. C. Santry, Can. J. Phys. **50**, 619 (1972).

[6] J. L. Oddou, J. Berthier, P. Peretto, and M. Robin, Phys. Status Solidi b **45**, K139 (1971); and J. L. Oddou, J. Berthier, and P. Peretto, Phys. Status Solidi b **51**, K67 (1972).

[7] J. Golczewski (private communication).

[8] R. P. Livi, F. P. Livi, J. D. Rogers, and F. C. Zawislak (unpublished).

[9] In Ref. 6, single Ni crystals were grown from the impurity bearing melt; however, the sensitivity of the channeling technique (using Rutherford backscattering) is not sufficiently great to study a uniformly distributed dilute (<0.001-at.%) impurity.

[10] See, for example, B. I. Deutch, in *Hyperfine Interactions in Excited Nuclei*, edited by G. Goldring and R. Kalish (Gordon and Breach, London, 1971), p. 137 and references therein; R. B. Alexander, N. J. Stone, D. V. Morgan, and J. M. Poate, in *Hyperfine Interactions in Excited Nuclei*, edited by G. Goldring and R. Kalish (Gordon and Breach, London, 1971), p. 229.

[11] H. E. Schiøtt, in *Ion Implantation*, edited by F. H. Eisen and L. T. Chadderton (Gordon and Breach, London, 1971), p. 197.

[12] R. B. Alexander and J. M. Poate, Radiat. Eff. **12**, 211 (1972).

[13] F. H. Eisen and E. Uggerhøj, Radiat. Eff. **12**, 233 (1972); R. B. Alexander, Report No. AERE-R-6849, July, 1971 (unpublished).

[14] J. U. Andersen, O. Andreasen, J. A. Davies, and E. Uggerhøj, Radiat. Eff. **7**, 25 (1971).

[15] J. U. Andersen, E. Laegsgaard, and L. C. Feldman, Radiat. Eff. **12**, 219 (1972).

[16] J. Lindhard, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. **34**, No. 14 (1965); J. U. Andersen and E. Laegsgaard, Radiat. Eff. **12**, 3 (1972).

[17] L. C. Northcliffe and R. F. Schilling, Nucl. Data Tables **7**, 233 (1970).

[18] Oxide-layer thickness was estimated from the host surface-peak area in the energy spectra, the result agreeing with previous experience with Ni samples identically treated.

[19] R. Reinbach, Z. Metallkd. **51**, 292 (1960).

[20] A. G. Guy, *Physical Metallurgy for Engineers* (Addison-Wesley, Reading, Mass., 1962), Chap. 9.

[21] We omit consideration here of a result of Ref. 6 in which impurity implantation (at a low energy of 40 keV) into a Ni single crystal was employed, because a large fraction of the implanted ions channeled along ⟨110⟩ axes. The results showed substantial additional interactions, possibly quadrupolar, and a large zero-field fraction.

[22] R. B. Alexander, E. Ansaldo, B. Deutch, and L. C. Feldman (unpublished).

[23] F. Abel, H. Bernas, M. Bruneaux, C. Cohen, and M. Thomé (unpublished).

PHYSICAL REVIEW B VOLUME 7, NUMBER 3 1 FEBRUARY 1973

Ligand Electron-Nuclear Double Resonance of Mn^{2+} in CdF_2[†]

Edward Y. S. Lee,[*] William J. Plant,[‡] Nak Sam Chung, and Robert Lee Mieher

Department of Physics, Purdue University, Lafayette, Indiana 47907

(Received 7 August 1972)

Electron-nuclear double-resonance (ENDOR) measurements have been obtained for the second, third, and fourth shells of fluorine lattice nuclei in CdF_2:Mn^{2+} with the dc magnetic field oriented along the three high-symmetry crystalline directions. ENDOR signals from the two cadmium isotopes have also been observed. Such cadmium ENDOR signals are believed to be the first observed in a CdF_2 lattice. Hyperfine constants for the three shells of fluorine nuclei around the Mn^{2+} defect have been obtained by fitting a simplified axial Hamiltonian. Using a more general Hamiltonian, the hyperfine constants for the two isotopes of the first shell of cadmium have also been obtained.

I. INTRODUCTION

In the CdF_2 lattice, Zaripov and co-workers made a series of electron-paramagnetic-resonance (EPR) studies of iron-group ions in CdF_2.[1] Mitrofanov *et al.* made a fluorine electron-nuclear double-resonance (ENDOR) study of V^{3+} in CdF_2.[2] Borcherts and Lohr[3] also studied V^{3+}, V^{2+}, and Cr^{3+} in CdF_2 using EPR and they used central-ion ENDOR to identify the V^{3+} ion. EPR and infrared studies were done by Eisenberger and Pershan[4] on both the insulating and semiconducting[5] CdF_2 crystals. Borcherts and co-workers[6] used EPR and ENDOR to study Gd^{3+} in CdF_2; they observed fluorine ligand ENDOR but not the cadmium ligand ENDOR. Ligand ENDOR on fluorine lattice nuclei were also observed by Valentin[7] in CdF_2: Eu^{2+}.

The EPR of Mn^{2+} in CdF_2 was first observed by Hall, Hayes, and Williams[8] during a study of Mn ions in various crystals. More recent EPR studies have been made by Ranon and Stamires[9] and by Richardson, Lee, and Menne.[10] These studies used both X-band and K-band spectrometers to determine the first-shell fluorine hyperfine constants by analyzing the superhyperfine structure observed in the Mn^{2+} EPR spectra.

We shall present ligand ENDOR data for both fluorine and cadmium lattice nuclei in CdF_2: Mn^{2+}