Magnetic hyperfine interaction studies of isolated Ni impurities in Pd and Pd-Pt alloys

W. Müller, H. H. Bertschat, H. Haas, B. Spellmeyer, and W.-D. Zeitz
Hahn-Meitner-Institut Berlin GmbH, Bereich Kern- und Strahlenphysik, D-1000 Berlin 39, West Germany
(Received 27 March 1989)

The magnetic hyperfine fields at isolated Ni impurities in Pd and Pd-Pt alloys were studied with the perturbed-angular-distribution (PAD) method by measuring the temperature, magnetic field, and concentration dependence of the nuclear-spin Larmor precession of isomeric states in ^{63}Ni. The recoil-implanted Ni nuclei, as products of heavy-ion nuclear reactions, are present in extreme dilution (<1 ppm) in the hosts. The positive Larmor frequency shift (Knight shift) observed for Ni impurities in Pd follows a Curie-Weiss-like temperature dependence with a large Curie constant indicating a giant moment behavior. For Ni impurities in the Pd-Pt alloys a considerable positive shift remains even at 30 at. % Pt content. The variation of the shift with Pt concentration and temperature reflects the variation of the Pd-Pt alloy susceptibility. The different contributions to the hyperfine field could be differentiated by comparing the Knight shift for Ni in Pd with its susceptibility contribution obtained from extrapolated susceptibility measurements in dilute Pd-Ni alloys. The negative core-polarization field of the impurity spin moment is compensated for by a transferred hyperfine field correlated with the host polarization in the neighborhood of the impurity. The remaining positive hyperfine field is due to a weak orbital moment of $0.3\mu_B$ at the impurity site. The values obtained for the different contributions are compared with results of the Korringa-Kohn-Rostoker–coherent-potential-approximation calculations for concentrated Pd-Ni alloys extrapolated to the dilute limit.

I. INTRODUCTION

For magnetic 3*d* transition-element impurities, such as Co and Fe in metals, usually negative hyperfine fields are found. The orbital moment is quenched in the metallic environment and the core polarization due to the remaining spin magnetism is responsible for the negative fields. Ni impurities appear to be nonmagnetic in most of the metallic hosts, and only a weak temperature-independent Knight shift at the impurity site is observed.[1,2] The Ni and Co hyperfine fields in the Pd host, however, show a remarkable anomaly. While the hyperfine fields in ferromagnetic Pd-Fe alloys are negative over the whole concentration range,[3] they increase to large positive values with increasing Pd content in Pd-Co and Pd-Ni alloys. They change their signs at 70 and 50 at. % Pd content and reach values of 26 and 20 T in the dilute limit for Pd-Co and Pd-Ni alloys, respectively.[4–6]

In Pd, which is near the borderline of magnetic ordering, a local 4*s*-electron polarization is induced at the impurity site by the polarized impurity and host *d* electrons in its neighborhood. This polarization can substantially contribute to hyperfine interactions. The existence of such a transferred hyperfine field[7,8] was therefore proposed by various authors to be the origin of the anomaly.[4,5,9,10] Experimental evidence for a positive transferred field was obtained especially from Mössbauer experiments in dilute Pd-Ni alloys.[10]

From the systematics of transferred hyperfine fields, however, it seems to be quite implausible that this field alone should compensate the negative core-polarization field and build up the large positive field: a drastic change to extremely large transferred fields would have to be assumed going from Mn and Fe to Co and Ni. Therefore another mechanism leading to positive fields, the formation of orbital moments, should also be considered.

There is theoretical and experimental evidence for orbital contributions to the magnetic moments in these systems. Theoretical predictions for the different hyperfine-field contributions in ferromagnetic Pd-Ni alloys stem from band-structure calculations using the Korringa-Kohn-Rostoker–coherent-potential-approximation (KKR-CPA) method.[11] Core-polarization and transferred hyperfine fields are obtained from the calculated local *d*-electron and *s*-electron spin densities. Within these calculations the change of sign of the hyperfine field with increasing Pd content is attributed to the concentration dependence of the transferred field. But, in order to obtain an agreement of the predicted overall saturation hyperfine field with experimental results, an additional orbital contribution has to be assumed. By parametrizing this contribution within an effective *g*-factor formalism, reasonable agreement with *g*-factor measurements from ferromagnetic-resonance (FMR) and neutron-diffraction experiments is obtained.[12,13] The occurrence of weak orbital moments due to the spin-orbit coupling accompanied by considerable positive hyperfine-field contributions has recently been demonstrated for the ferromagnetic metals Fe, Co, and Ni in a fully relativistic calculation by Ebert *et al.*[14] Experimental hints for orbital magnetism are also extracted from NMR experiments observing broad hyperfine-field distributions in Pd-Fe-Ni, Pd-Co, and Pd-Fe-Co alloys,[6,15] as well as from the observation of magnetocrystalline anisotropy and anisotropies in the magnetostriction and magnetoresistance in fer-

romagnetic crystals of these alloys.[16–19]

Orbital contributions to the magnetic hyperfine field of $3d$-element impurities are known in some other cases. A weak, temperature-independent, and positive Knight shift of Ni impurities in the noble metals are analyzed in terms of the d-electron orbital susceptibility.[2] The large positive Knight shift of Fe impurities in Ca and Co impurities in Au are taken as indication of localized orbital moments.[20,21] For the extreme impurity host combinations of Ni and Fe atoms in alkali metals, the observed positive hyperfine fields even agree with the large fields calculated for spin-orbit-coupled ionic $3d^9$ and $3d^6$ configurations.[22,23] These findings are connected with the fundamental problem under which conditions and to what extent ionic configurations of the d electrons screening the local impurity potential can survive the hybridization with the conduction-electron orbitals in the metallic host. In addition, these configurations might be modified by crystal-field effects and spin-orbit coupling.

In this respect the magnetic behavior of the isolated Ni impurity in Pd deserves special attention.[24] However, most of the investigations on Pd-Ni alloys deal with Ni concentrations near or above the critical concentration for the onset of ferromagnetism. Hitherto, no direct experimental information about the behavior of the isolated impurity was available. Susceptibility and magnetization,[25] neutron diffraction,[26] and the Mössbauer experiments[10] have indicated that large magnetic inhomogeneities are present in dilute Pd-Ni alloys. From some of these measurements, nonmagnetic behavior of the isolated Ni impurity was asserted, whereas the predominant role in the formation of the ferromagnetic state was attributed to small magnetic Ni clusters.

In order to get further insight into the magnetic behavior and hyperfine-field contributions of isolated Ni impurities in Pd, we carried out measurements of the temperature and magnetic field dependence of the magnetic hyperfine field via the perturbed-angular-distribution (PAD) method utilizing two isomeric levels in ^{63}Ni. This technique, applied in combination with heavy-ion nuclear reactions used to produce and implant the probe isotopes, allows measurements over a wide range of temperatures with a probe-nuclei concentration well below 1 ppm. In such extreme dilution, even the magnetic $3d$ impurities in Pd can be regarded as isolated.[27] In this paper we report about the observation of a large, positive, and strongly-temperature-dependent Knight shift of the isolated Ni impurity in Pd. In an experiment with a single-crystal sample we checked for and found no anisotropy of the hyperfine field. We demonstrate that an orbital hyperfine field as well as a positive transferred field due to the considerably polarized Pd environment have to be assumed to reproduce the observed Knight shift. The measured relaxation rates of the probe nuclear-spin alignment agree with estimates assuming an orbital hyperfine field and a small spin-fluctuation temperature. A considerable decrease in the Ni Knight shift occurs upon alloying Pt to the Pd samples. However, at higher Pt concentration a positive shift still remains. We suggest that the dependence of the Ni Knight shift on Pt concentration in the Pd-Pt alloy may be qualitatively understood as a consequence of transferred fields. In the following section we give a brief review of our experimental technique.

II. EXPERIMENTAL TECHNIQUE

The time-differential measurement of the perturbed angular distribution, a well-established method in nuclear physics with various applications to solid-state physics, has been used in our experiment.[28,29] In PAD measurements the variation of the anisotropic distribution of γ rays emitted from deexciting isomeric states of aligned nuclei is being observed. ^{18}O beam pulses of 45 meV, width of 1 ns, and a repetition time of 2 μs, provided by the heavy-ion accelerator facility VICKSI at the Hahn-Meitner-Institut (Berlin), are used to populate the isomers via the compound nuclear reaction ^{48}Ca(^{18}O,3n)^{63}Ni in a thin ^{48}Ca foil (1 mg/cm^2). The produced Ni nuclei are strongly aligned. The alignment is seen in the decay of the $\frac{9}{2}^+$ and $\frac{5}{2}^-$ isomeric states of ^{63}Ni that we use for the measurements. Part of the ^{63}Ni level scheme is shown in Fig. 1. The recoil energy of about 12 meV is sufficient for the Ni nuclei to leave the Ca foil and to be implanted up to a depth of 10^4 Å into the Pd, Pt, and Pd-Pt samples directly behind the foils.

Because of the similarities in the electronegativities, chemical potentials, electron densities, and atomic radii of the isoelectronic impurity and hosts, substitutional lattice sites can be assumed as final resting places of the implanted atoms. This assumption is supported by alloying rules, like the Hume-Rothery or the Miedema rules.[30] Even from pure collisional arguments,[31] we calculate that 80% of the Ni atoms come to rest with a replacement collision in the Pd host. The nearest-neighbor environment of the impurity is likely to be unperturbed by radiation damage because the probability for the formation of a neighboring vacancy is very small.[32] The electronic re-

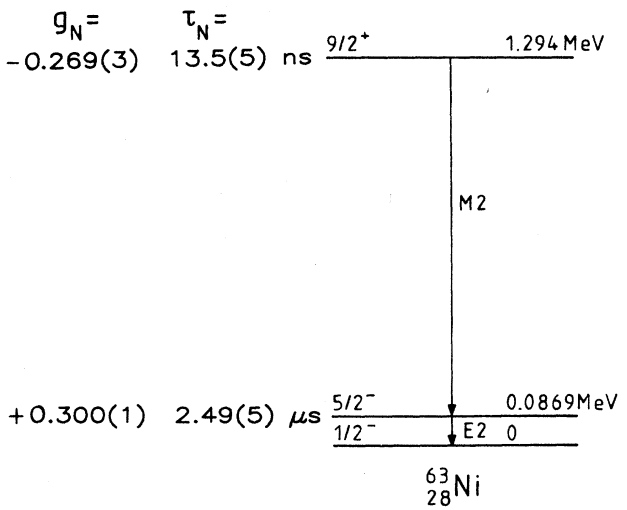

FIG. 1. Scheme of low-lying levels in ^{63}Ni. Nuclear g factors, lifetimes, and γ energies of the $\frac{5}{2}^-$ and $\frac{9}{2}^+$ isomeric states are also given. Details of the nuclear properties will be published elsewhere (Ref. 35).

laxation processes in metallic hosts are short ($<10^{-12}$ s) compared to the lifetimes τ_N of the isomeric states, and therefore the measurement starts in a well-defined electronic equilibrium configuration. The concentration of the implanted Ni atoms remains well below 1 ppm during the measurement.

An external magnetic field B_{ext} was applied perpendicular to the plane defined by the ion-beam direction and the γ-ray detector axes. In the effective local magnetic field B_{eff}—external field B_{ext} and induced internal magnetic hyperfine field $\langle B_{\text{hf}} \rangle$—the anisotropic γ-ray distribution precesses around the direction of B_{eff} with the Larmor frequency ω_L:

$$\omega_L = -\hbar^{-1} g_N \mu_N (B_{\text{ext}} + \langle B_{\text{hf}} \rangle) \ . \tag{1}$$

Here, g_N is the nuclear g factor and μ_N is the nuclear magneton. As a consequence, the γ-ray intensity $I(\theta,t)$, which is recorded as a function of time between the beam pulses, is modulated by the frequency ω_L, and for the given experimental arrangement we obtain

$$I(\theta,t) = I_0 e^{-t/\tau_N} \sum_{k=0,2,4} G_k(t) A_k B_k P_k(\cos(\theta - \omega_L t)) \ . \tag{2}$$

θ is the angle between the detector axis and the ion-beam direction. The orientation parameters B_k specify the strength of the initial alignment in the nuclear reaction, the directional distribution coefficients A_k reflect the transition probabilities involved in the γ decays, and the P_k are Legendre polynomials.

Additional hyperfine interactions such as fluctuations in the magnetic hyperfine field, a static electric-field-gradient distribution caused by radiation damage in the vicinity of the probe nucleus, and static magnetic hyperfine field distributions in the alloys may produce an attenuation of the initial alignment. This effect is included in Eq. (2) by multiplying with the appropriate attenuation functions $G_k(t)$.

Taking ratio functions of the normalized time spectra from two detectors,

$$R(t) = \frac{I(\text{Det1},\theta,t) - I(\text{Det2},\ \theta+\pi/2,\ t)}{I(\text{Det1},\theta,t) + I(\text{Det2},\ \theta+\pi/2,\ t)}$$

$$\approx \tfrac{3}{4} G_2(t) A_2 B_2 \cos(2(\theta - \omega_L t)) \ , \tag{3}$$

we extract the spin-rotation patterns, which are shown as typical examples in Figs. 2 and 3. The Knight shift $K = \langle B_{\text{hf}} \rangle / B_{\text{ext}}$ is now extracted from the measured Larmor frequencies according to $K = (\omega_L - \omega_{\text{ref}})/\omega_{\text{ref}}$, where the applied magnetic field is determined from the Larmor frequency ω_{ref} of Ni nuclei in a reference substance with negligible Knight shift.

Following the work of Micha,[33] we briefly discuss the attenuation, which is due to a fluctuating magnetic field $\mathbf{B}(t)$ coupled to the nuclear spin $\mathbf{I}$ via the Hamiltonian $H = -g_N \mu_N \mathbf{I} \cdot \mathbf{B}(t)$. The fluctuations may be characterized by the correlation time τ_C and the mean square of the magnitude of the fluctuating field $\langle |B(0)|^2 \rangle$. The

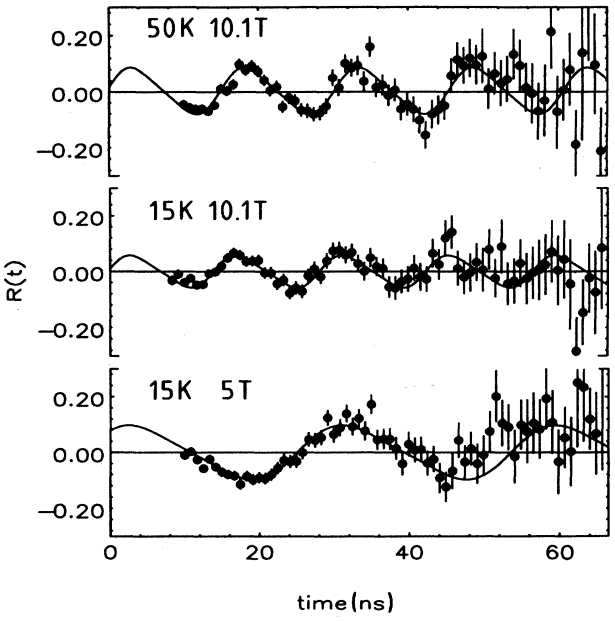

FIG. 2. Spin-rotation patterns from the $\frac{9}{2}^+$ isomer for Ni in Pd, measured at indicated temperatures and external magnetic fields. Since the angle between the detectors was larger than $\pi/2$, corrections due to the $k=4$ term in Eq. (2) were included, fitting the spin-rotation patterns.

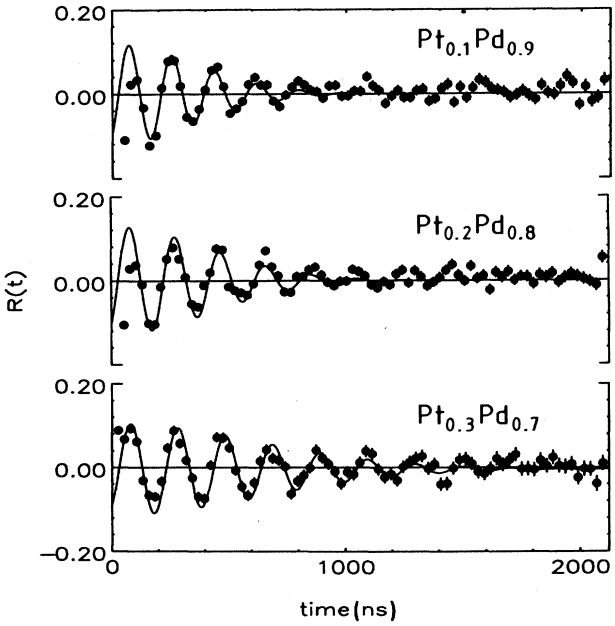

FIG. 3. Spin-rotation patterns from the $\frac{5}{2}^-$ isomer for Ni in Pd-Pt alloys at various Pt concentrations ($T=150$ K and $B_{\text{ext}}=1.0$ T). Note the decreasing damping of the amplitude in the spin-rotation patterns with increasing Pt content.

loss of the initial alignment is then described by the attenuation factor

$$G_k(t)=e^{-\lambda_k t}, \tag{4}$$

with

$$\lambda_k=\tfrac{1}{3}\tau_C\omega_C^2 k(k+1), \tag{5}$$

and $\omega_C=-\hbar^{-1}g_N\mu_N\langle|B(0)|^2\rangle^{1/2}$. If a local electronic moment is formed at the impurity site, its paramagnetic fluctuations dominate the fluctuations in the local field. These paramagnetic fluctuations are often mediated via exchange coupling to the conduction electrons in the metallic host. Above the intrinsic spin-fluctuation temperature the fluctuation rate τ_C^{-1} then follows a Korringa law, i.e., is linear with temperature and from Eq. (5) the nuclear relaxation rate λ_k is proportional to the inverse temperature. However, any interpretation of nuclear relaxation rates obtained by PAD measurements within the framework of magnetic fluctuations has to be checked very carefully: The interaction of the nuclear quadrupole moment with a field-gradient distribution produced by radiation damage might cause attenuations quite similar to the relaxation from dynamical magnetic interactions.[32,34]

High magnetic fields up to 10 T were provided by the superconducting split-pair magnet SULEIMA.[36] The γ rays were detected with NaI(Tl) detectors and the time spectra were recorded with a standard fast-slow-coincidence technique. For temperature variation the samples were mounted on the copper cold tip of a helium continuous-flow cryostat. The temperature was controlled via a platinum resistor and measured by a carbon resistor. A capacitance thermometer for which even very high magnetic fields have no influence on the capacitance-versus-temperature characteristic was used for calibration.[37]

We used high-purity (99.999%) Pd and Pt disks for the pure-element samples. The sample contamination with Ni was 2 ppm and the contamination with Mn, Fe, and Co less than 4 ppm by weight. The Pd-Pt alloys were prepared by rf induction melting the appropriate amounts of the pure constituents in an aluminum oxide crucible. After rolling the buttons to thin plates, the samples were annealed for 4 h by induction heating at 1720 K and quenched to room temperature. The homogeneity of the alloys was tested by electron-microprobe analysis. For the single-crystal experiments disks were cut parallel to the (110) plane from a 5-mm-diam single-crystal rod (99.99% pure) of Pd. The disks were aligned by x-ray diffraction and fixed on the copper cold finger with either the [111] or the [100] axes parallel to the external field. The target material calcium was enriched 96% with the isotope ^{48}Ca.

III. EXPERIMENTAL RESULTS

The magnetic behavior of isolated Ni impurities in Pd and Pd-Pt alloys as it is reflected in the temperature, magnetic field, and concentration dependences of the magnetic hyperfine field is shown in Figs. 4 and 5. The

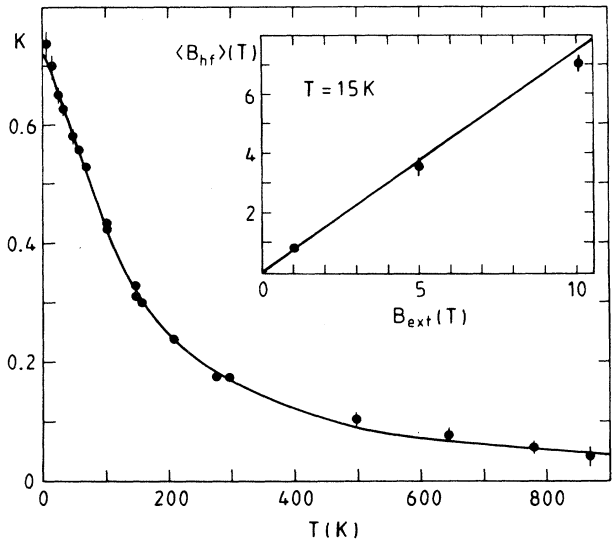

FIG. 4. Knight shifts $K=\langle B_{\rm hf}\rangle/B_{\rm ext}$ at various temperatures for isolated Ni impurities in Pd. The solid line is obtained fitting Eq. (11) to the data. The inset shows the dependence of the induced hyperfine field on the external field at 15 K. The line indicates a linear relation.

plotted Knight shift $K=\langle B_{\rm hf}\rangle/B_{\rm ext}$ was calculated from the Larmor frequencies, where we have chosen the target material calcium as a convenient reference substance for the following two reasons. No temperature dependence of the Larmor frequency of isolated Ni impurities in Ca was found between 4 and 300 K. The Knight shift at

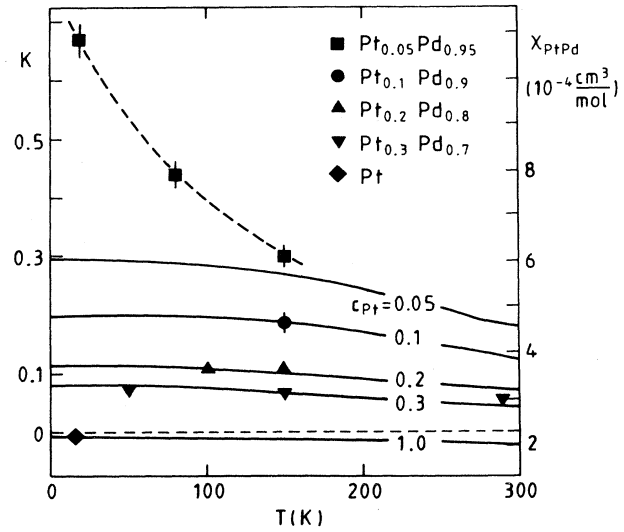

FIG. 5. Knight shifts for isolated Ni impurities in Pt and Pd-Pt alloys at various temperatures and Pt concentrations. The solid lines show the temperature dependence of the Pd-Pt alloy susceptibilities (Ref. 39). The scale of the susceptibility data was adjusted to fit the Knight shift at 150 K and $c_{\rm Pt}=10$ and 30 at. %. The dashed lines are inserted to guide the eye.

room temperature is very small: $-0.7(5)\%$, the error reflecting the uncertainty in the g factor of the $\frac{5}{2}^-$ isomer.[38] Compared with the large Knight shifts observed in the Pd and Pd-Pt matrices, we can neglect the minor shift in Ca. In all measurements well-defined Larmor frequencies were observed and the spin-rotation amplitude was preserved over the whole temperature range. Both experimental facts indicate that only a negligible number of probe atoms are associated with radiation defects located in the nearest neighborhood.

The temperature dependence of the Knight shift for the isolated impurity in the pure Pd host is depicted in Fig. 4. A large positive Knight shift is seen with a Curie-Weiss-like temperature dependence. Parametrizing the data in the simple form

$$K(T)=\frac{C}{3k_B(T+\Theta)}\ , \tag{6}$$

$\Theta=35$ K and $C=266\mu_B$T are obtained. The magnitude of the Curie constant is considerably larger than observed in most hyperfine-field measurements for $3d$ elements in metallic hosts; for example, of Fe impurities in the noble metals.[29] This indicates a substantial contribution of the polarized Pd host to the magnetic moment of the isolated impurity. A detailed discussion of the different hyperfine-field contributions hidden in the observed Knight shift will be given in the following section. Below 35 K the Knight shift deviates from the Curie-Weiss law. There remains, however, an essentially linear dependence of the induced hyperfine field on the external field up to values of $B_{\rm ext}=10$ T (Fig. 4, inset) in this temperature range.

The isotropy of the hyperfine field of the paramagnetic Ni impurity was tested by implanting the probe nuclei into a Pd single crystal. We measured the frequency at 50, 100, and 150 K with the external field in the direction of the [111] and [100] crystal axes, respectively. In all cases the relative difference in the fitted Knight shifts, $\Delta K/K$, was smaller than 2%, within the systematic error of our experiment.

The data for the Knight shift of the Ni impurity in the Pd-Pt alloy are shown in Fig. 5 for various Pt concentrations including pure Pt. The strong variation with temperature of K observed for Ni in Pd-rich alloys is reduced with increasing Pt content. But even at 30 at. % Pt content, there remains a considerable positive shift of $K\approx 0.07$. In order to compare the concentration and temperature dependence of the Knight shift with the behavior of the Pd-Pt alloy susceptibility, we include plots of susceptibility data[39] in Fig. 5. The scale for the susceptibility is adjusted to fit the Knight shift at 150 K, 10 and 30 at. % Pt. Figure 5 gives the clear indication that above 10 at. % Pt concentration the variation with temperature and concentration of the impurity hyperfine field scales with the variation of the host magnetization.

Next, we consider the relaxation of the nuclear alignment observed for the probe nuclei in the pure Pd matrix. The relaxation seen in the rotation pattern for the $\frac{5}{2}^-$ isomer was fitted with the attenuation function [Eq. (4)] typical for a fluctuating magnetic field causing the relaxation. A linear relation is obtained between the fitted relaxation rate and the inverse temperature (Fig. 6), which is indeed expected if fluctuating local electronic moments coupled to conduction electrons cause the relaxation of the alignment. In the low-temperature spin-rotation pattern of the $\frac{9}{2}^+$ isomer, no relaxation is seen even at 4 K within the time window available. Therefore the relaxation rate for the $\frac{5}{2}^-$ isomer as function of $1/T$ has to saturate at an estimated value of $\lambda_2(\frac{5}{2}^-)<5\times 10^6\ {\rm s}^{-1}$.

Interesting features are seen in the damping of the spin-rotation patterns obtained for the probe nuclei in the Pd-Pt alloys (Fig. 3). The damping function has a Gaussian form rather than the Lorentzian form of Eq. (4). Therefore, we fitted the patterns with the appropriate attenuation factor for a static hyperfine-field distribution. The widths obtained for the Gaussian frequency distribution at 150 K are plotted as a function of the Pt concentration as an inset in Fig. 6. At low Pt concentrations the damping is quite large compared with the relaxation observed in pure Pd, and it decreases drastically with increasing Pt content.

IV. INTERPRETATION

A. The different hyperfine-field contributions for Ni impurities in Pd

We analyze the different hyperfine-field contributions for the isolated Ni impurity in Pd by comparing the Knight-shift data with the susceptibility contribution of the isolated impurity. Susceptibility measurements for Pd-Ni alloys at very low Ni concentrations ($c=0.2$, 0.5, and 1 at. %) were performed by Chouteau and coworkers.[40,41] In this concentration range the susceptibili-

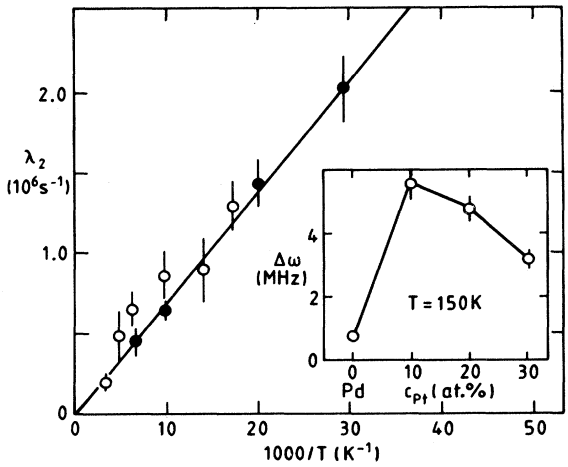

FIG. 6. Relaxation rates of the spin alignment of the $\frac{5}{2}^-$ isomer of Ni in Pd (open symbols, polycrystalline samples; solid symbols, Pd single crystal). The inset shows the dependence of the width of the Gaussian frequency distribution on Pt concentration, fitting the damping of the spin-rotation pattern for Ni in Pd-Pt alloys at 150 K. The value for pure Pd corresponds to the Lorentzian distribution width according to Eq. (4).

ty contribution of the Ni atom, $\Delta\chi$—obtained from the measured susceptibilities of the alloy χ_{alloy} and the pure host χ_{Pd} according to $\Delta\chi=[\chi_{\text{alloy}}-(1-c)\chi_{\text{Pd}}]/c$—becomes independent of the concentration, and a reasonable extrapolation can be made to the susceptibility of the isolated impurity.

In the low-concentration range, $\Delta\chi$ shows a large exchange enhancement that is due to the embedding of the magnetic impurity in the strongly polarizable Pd host. In order to support the analyses we shall give for the hyperfine-field contributions, we briefly discuss the exchange enhancement following the molecular-field model of Takahashi and Shimizu,[42] thereby fixing our notation. Not only the magnetization of the bare impurity spin $\langle\mu_{\text{Ni}}^S\rangle$ and some orbital contribution $\langle\mu_{\text{Ni}}^L\rangle$ of the $3d$ electrons, but also the polarization of the neighboring Pd spins in the molecular field $\alpha\langle\mu_{\text{Ni}}^S\rangle$ of the impurity spin contribute to the total observed magnetization per Ni atom $\langle\mu_{\text{tot}}\rangle=\Delta\chi B_{\text{ext}}$, which is then given by $\langle\mu_{\text{tot}}\rangle=(1+\alpha\chi_{\text{Pd}})\langle\mu_{\text{Ni}}^S\rangle+\langle\mu_{\text{Ni}}^L\rangle$. The interaction between the localized spin and the $4d$ band of the Pd host is described by the molecular-field constant α.

The orbital contribution to the magnetic moment can be neglected compared to the quite large overall spin moment:

$$\langle\mu_{\text{tot}}\rangle\approx(1+\alpha\chi_{\text{Pd}})\langle\mu_{\text{Ni}}^S\rangle\ . \tag{7}$$

Consequently, the magnetic behavior of the alloys is generally discussed assuming pure spin magnetism. However, such a point of view is not admitted as far as hyperfine-field contributions are concerned. Even a very weak orbital moment can contribute substantially to the total magnetic hyperfine field.[14] The magnetization $\langle\mu_{\text{Ni}}^S\rangle$ is not only induced by the external field, but also by the molecular field $\alpha\chi_{\text{Pd}}B_{\text{ext}}$, which is due to the Pd neighbors seen by the impurity spin. Enhancement effects can therefore be included in the susceptibility $\Delta\chi$ by substituting an effective g factor $(1+\alpha\chi_{\text{Pd}})g_S$ for the bare-spin g factor g_S.

With these ideas in mind, we distinguish three different hyperfine-field contributions comprising the total hyperfine field $\langle B_{\text{hf}}\rangle=\langle B_c\rangle+\langle B_L\rangle+\langle B_s\rangle$ at the Ni impurity.

(1) A core-polarization field $\langle B_c\rangle$ is caused by the Fermi-contact interaction of electrons of inner closed s shells, which are polarized by the spin of the $3d$ electrons in the same ion. From Hartree-Fock calculations and experimental data, we can estimate the contact field per unpaired d electron[43] to be

$$\langle B_c\rangle=-12.5\,\text{T}/\mu_B\langle\mu_{\text{Ni}}^S\rangle\ . \tag{8}$$

(2) Following the analysis of Akai,[11] we parametrize the orbital contribution $\langle B_L\rangle$ as a shift Δg of the spin g factor g_S:

$$\langle B_L\rangle=2\mu_B\langle r^{-3}\rangle(\Delta g/g_S)\langle\mu_{\text{Ni}}^S\rangle\ . \tag{9}$$

Extrapolation of Hartree-Fock results[43] for the expectation value of the inverse cube of the distance between a $3d$ electron and the nucleus results in $\langle r^{-3}\rangle=6.4$ a.u., and thus $2\mu_B\langle r^{-3}\rangle=80\,\text{T}/\mu_B$. In the ansatz [Eq. (8)] a strong coupling between spin and orbital moment is assumed similar to the mechanism suggested for the CoAu system.[20]

(3) Finally, we include the transferred hyperfine field $\langle B_s\rangle$ following the analysis of the Mössbauer data.[10] The field is caused by the contact interaction of impurity $4s$ orbitals polarized essentially by the hybridization with spin-polarized d orbitals of neighboring host atoms.[8] Therefore we may assume the transferred field to be proportional to the host polarization in the neighborhood of the impurity. This assumption is supported by the behavior of the Knight shift of Ni in the Pd-Pt alloys, where the same dependence on temperature and Pt concentration is seen as for the host susceptibility. Let B_{tr} be the hyperfine field transferred per μ_B magnetization localized in the shell of the 12 Pd nearest-neighbor atoms of the Ni impurity. This magnetization is some fraction, k, of the total host magnetization induced by the molecular field of the impurity spin. In addition, we take into account the polarization of the nearest-neighbor Pd atoms by the external field. Including both contributions, we can write

$$\langle B_s\rangle=B_{\text{tr}}k\alpha\chi_{\text{Pd}}\langle\mu_{\text{Ni}}^S\rangle+12B_{\text{tr}}\chi_{\text{Pd}}B_{\text{ext}}\ . \tag{10}$$

Summing up all hyperfine-field contributions and using the approximation (7), we introduce the following parametrization of the Knight shift in terms of impurity and host susceptibility:

$$K=\left[-12.5\frac{\text{T}}{\mu_B}+80\frac{\text{T}}{\mu_B}\left[\frac{\Delta g}{g_S}\right]+B_{\text{tr}}k\alpha\chi_{\text{Pd}}\right]\frac{\Delta\chi}{1+\alpha\chi_{\text{Pd}}}+12B_{\text{tr}}\chi_{\text{Pd}}\ . \tag{11}$$

The unknown parameters for the isolated impurity are the orbital contribution and the transferred field. The values of the other parameters may be obtained from available measurements and calculations: We have taken $\Delta\chi$ from the data of Chouteau and co-workers.[40,41] They obtained $\alpha=4900$ mol/emu and for the bare spin of the Ni atom, $\mu_{\text{Ni}}^S=0.7\mu_B$, from their susceptibility data, which gives a total moment of $\mu_{\text{tot}}=3\mu_B$. The Pd susceptibility was interpolated between the low-temperature data of Chouteau[40] and the high-temperature data of Kojima *et al.*[44] fitting nicely at room temperature. A microscopic picture of the spin structure for $3d$ impurities embedded in the polarized Pd environment was obtained from cluster calculation by Oswald *et al.*[45] The calculation was carried out for $3d$ impurities within an extended cluster of Pd atoms. From the results, one can conclude that a large fraction, $k\approx\frac{1}{3}$, of the induced Pd polarization is localized within the nearest-neighbor shell of the Ni impurity.

The parameters Δg and B_{tr}, which determine the orbital contribution and the transferred hyperfine field, are obtained by fitting Eq. (11) to the measured Knight-shift data. The solid line in Fig. 4 shows the best fit, giving $\Delta g=0.8(1)$ and $B_{\text{tr}}=+7.5(1)\,\text{T}/\mu_B$. As can be seen

from Fig. 4, the temperature dependence of the Knight shift is described over the whole temperature range within the simple molecular-field model.

On the basis of these elaborations, the different contributions to the saturation hyperfine field may be estimated. In Fig. 7 the results are plotted, together with the calculated hyperfine-field contributions given by Akai[11] for ferromagnetic Pd-Ni alloys as a function of the Ni concentration. In the dilute limit the core-polarization field essentially cancels the positive transferred field, and the saturation hyperfine field is predominantly determined by the orbital contribution of a weak orbital moment of $0.3\mu_B$. The error bars indicate the uncertainties arising from different values for μ_{tot} and α given in the literature. In view of these uncertainties, the agreement obtained with the values from the band-structure calculations for ferromagnetic Pd-Ni alloys extrapolated to the low-concentration limit is to be considered excellent.

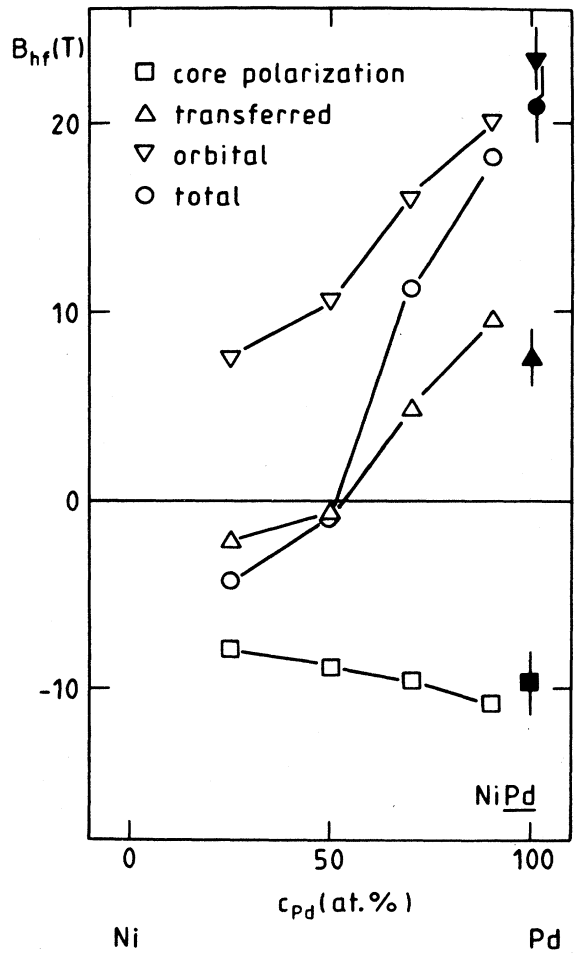

FIG. 7. The contributions to the saturation hyperfine field for Ni in Pd-Ni alloys: calculated for ferromagnetic alloys in Ref. 11 (open symbols) and extracted from the temperature dependence of the Knight shift for isolated Ni impurities in Pd (solid symbols). Core polarization fields (squares), transferred fields (triangles), and orbital fields (reversed triangles) form the total hyperfine fields (circles).

B. Relaxation behavior of the alignment for Ni in Pd and Pd-Pt alloys

We now focus on the relaxation of the nuclear alignment observed for the probe nuclei in the Pd and Pd-Pt alloys. For Ni in pure Pd the relaxation rate is proportional to the inverse temperature. This experimental result clearly indicates the predominance of paramagnetic relaxation processes. Indeed, we expect the radiation-damage effect to be small: the strength of the quadrupole damping was measured for the case of recoil-implanted Cd ions in Pd.[32] At 25 K a pure quadrupole rate of about $2\times10^6\ s^{-1}$ was observed. This is the same order of magnitude as seen in our experiment (Fig. 6). However, the quadrupole moment of the involved $\frac{5}{2}^+$ isomer in ^{111}Cd is 0.8 b, while for the $\frac{5}{2}^-$ isomer ^{63}Ni a small quadrupole moment well below 0.2 b is expected.[46] Therefore the pure quadrupole damping should be considerably smaller than the relaxation observed in our experiment.

Assuming that the fluctuations in the local field dominate the relaxation of the alignment, we expect the relaxation rate to saturate at low temperature due to the intrinsic spin fluctuations. For the upper limit of the saturation value, we have estimated $\lambda_2=5\times10^6\ s^{-1}$. On the other hand, the Korringa behavior of the relaxation rate down to 30 K (Fig. 6) indicates that the intrinsic spin-fluctuation temperature T_f, below which the saturation takes place, is considerably smaller than 30 K. From the uncertainty relation $\tau_C\approx\hbar/k_BT_f$, we therefore expect the correlation time of the spin fluctuation to be on the order of 1 ps. From these estimates of λ_2 and τ_C, the amplitude of the fluctuating local field may now be calculated according to Eq. (5), and a value of 100 T is obtained. This is in the range of fields for orbital hyperfine interactions of the $3d$ electrons, thus giving additional support to the assumption of orbital magnetism. The observed relaxation of the nuclear alignment may therefore be qualitatively understood as a consequence of orbital magnetism and a weak intrinsic spin-fluctuation temperature of the isolated Ni impurity in Pd.

In addition to the mentioned relaxation mechanism, the hyperfine-field distribution due to different environments of the impurity in the Pd-Pt alloy causes a damping of the spin alignment. For this damping, we expect indeed a Gaussian form, as is observed due to the distribution of the local fields. The width of the distribution should be largest at low Pt concentrations, where the nickel impurities still show a local-moment-like behavior including an orbital contribution, and where they are thus quite sensitive to the substitution of Pd atoms by Pt atoms in their neighborhood.

V. DISCUSSION

We have demonstrated that the results of our hyperfine-field measurements and extrapolated susceptibility data can be combined in a consistent way over the whole temperature range assuming orbital hyperfine fields as well as transferred fields. Clearly, the molecular-field model gives only a crude description of the electronic structure. However, it allows, in a quanti-

tative way, description of two main features of our data.

First, the Knight shift does not simply scale with the susceptibility contribution of the Ni atom. A considerable positive shift still remains at higher temperatures. This leads to the assumption of a transferred hyperfine field scaling with the host susceptibility. A similar conclusion was drawn from Mössbauer experiments in dilute Pd-Ni alloys.[10] The assumption is further experimentally supported by the observation of a positive Knight shift for the Ni impurities in the Pd-Pt alloys. With increasing Pt content the local-moment-like behavior of the Ni impurity breaks down, but a considerable positive Knight shift remains. At 20 and 30 at. % Pt its temperature and concentration dependence is essentially correlated with the Pd-Pt alloy host susceptibility. Therefore, in this concentration range the behavior of the impurity may be described by large intrinsic spin-fluctuation temperatures,[47] loss of orbital correlations, and hyperfine fields dominated by a positive transferred field.

Second, taking into account the negative core-polarization field, the positive transferred field alone cannot fully explain the observed saturation field. To fit our data over the whole temperature range, we have to allow for orbital contributions. Considering only a transferred field, a host polarization even much larger than that expected from the mentioned experimental and theoretical studies would not lead to satisfactory results. Furthermore, the observation of a strong relaxation of the nuclear alignment scaling with the inverse temperature down to 30 K supports the assumption of a large orbital field contributing to the fluctuating local field.

A deeper theoretical understanding of the hyperfine-field measurement needs a microscopic model in which orbital correlations are included. The available discussions of the magnetic behavior of $3d$ impurities in metallic hosts within the localized spin-fluctuation model[48] or the Anderson model[49] start with pure spin magnetism and hybridization effects. Until recently,[14] band-structure calculations also lack the treatment of orbital correlations. The calculation of orbital hyperfine fields is possible within the ionic model of Hirst,[50,51] but this model can only be applied in cases where hybridization effects in the metallic host are weak compared with orbital correlations and crystal fields. Often the predominance of hybridization effects is assumed for the Ni*Pd* system. The impurity is considered to be nonmagnetic and its properties are treated in a model of exchange-enhanced spin fluctuations.[48] However, the observed strong temperature dependence of the Knight shift and nuclear relaxation rate clearly demonstrates that the isolated Ni impurity in Pd is far from the nonmagnetic regime and near or even above the borderline of local-moment formation. The estimated spin-fluctuation temperature is well below 30 K. The observed anisotropies in the magnetic properties of Pd-Ni alloys also suggest the ionic model.[6,15,16]

Therefore one may presume that the ionic structure of a hole in the $3d$ shell of the Ni impurity survives the hybridization in the metallic host. Experimental support for a well-defined hole at the Ni site in dilute Pd-Ni alloys was recently given by Coleridge *et al.*[52] The ionic model then provides us with a microscopic justification for the ansatz (9). We describe the behavior of the Ni atom starting with a $3d^9$ configuration and treat the crystal field in the intermediate-coupling scheme. The ^2D, $L=2$, $S=\frac{1}{2}$ term splits in the cubic crystal field into the Γ_3 doublet and the Γ_5 triplet. For a fcc and bcc metallic environment, we expect the doublet to be lower.[50] Its magnetic behavior is approximately equivalent to the behavior of a spin doublet with completely quenched orbital degrees of freedom. However, we should take into account the spin-orbit coupling $H_{LS}=\lambda LS$, which is quite large for Ni ions at the end of the $3d$ group ($\lambda\approx -0.08$ eV). The spin-orbit coupling mixes some of the triplet into the ground state, causing an "unquenching" of the orbital moment and an orbital hyperfine-field contribution given by Eq. (9).[53] The g-factor shift is $-4\lambda/\Delta$, and we estimate for the crystal-field splitting $\Delta\approx 0.4$ eV, a reasonable order of magnitude for the elements of the $3d$ group.

A further splitting of the doublet might be caused by tetragonal distortions in the cubic symmetry, which would lead to considerable anisotropies in the g factor as well as in the hyperfine field.[53] A magnetocrystalline anisotropy was indeed observed in dilute ferromagnetic Pd-Ni alloys.[16] However, isotropy of the magnetic hyperfine field was observed within the accuracy of our measurements for isolated paramagnetic Ni impurities in a Pd single crystal. Therefore, we conclude that the anisotropy in the ordered phase of the alloys does not correspond to an anisotropy in the single-ion behavior. Clearly, the problem of the magnetocrystalline anisotropy in the low-spin, dilute Pd-Ni alloys has to be investigated further.

[1]A. Narath, in *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. 5, p. 149.
[2]L. Dworin and A. Narath, Phys. Rev. Lett. **25**, 1287 (1970).
[3]P. P. Craig, B. Mozer, and R. Segnan, Phys. Rev. Lett. **14**, 895 (1965).
[4]U. Erich, J. Göring, S. Hüfner, and E. Kankeleit, Phys. Lett. **31A**, 492 (1970).
[5]J. E. Tansil, F. E. Obenshain, and G. Czjzek, Phys. Rev. B **6**, 2769 (1972).
[6]M. Katayama, K. Kumagai, T. Kohara, K. Asayama, I. A. Campbell, N. Sano, S. Kobayashi, and J. Itoh, J. Phys. Soc. Jpn. **40**, 429 (1976).
[7]E. Daniel and J. Friedel, J. Phys. Chem. Solids **24**, 1601 (1963).
[8]J. Kanamori, Hyperfine Interact. **21**, 159 (1985).
[9]A. E. Balabanov, N. N. Delyagin, A. L. Yerzinkyan, V. P. Parfenova, and V. S. Shpinel, Zh. Eksp. Teor. Fiz. **55**, 2136 (1968) [Sov. Phys.—JETP **28**, 1131 (1969)].
[10]J. Fink, G. Czjzek, H. Schmidt, and F. E. Obenshain, in Progress Report No. KfK 2670, edited by K. Käfer (Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, 1978), p.

56; J. Fink, G. Czjzek, H. Schmidt, K. Tomala, and F. E. Obenshain, in *Transition Metals 1977,* IOP Conf. Ser. No. 39, edited by M. J. G. Lee, J. M. Perz, and E. Fawcett (IOP, London, 1978), p. 469.
[11]H. Akai, J. Phys. Soc. Jpn. **51**, 468 (1982).
[12]G. Fischer, A. Herr, and A. J. P. Meyer, J. Appl. Phys. **39**, 545 (1968).
[13]J. W. Cable and H. R. Child, Phys. Rev. B **1**, 3809 (1970).
[14]H. Ebert, P. Strange, and B. L. Gyorffy, J. Phys. F **18**, L135 (1988).
[15]Le Dang Khoe, P. Veillet, and J. A. Campbell, J. Phys. F **6**, L197 (1976).
[16]D. M. S. Bagguley and J. A. Robertson, J. Phys. F **4**, 2282 (1974).
[17]I. Mirebeau, M. Hennion, F. Hippert, and I. A. Campbell, J. Magn. Magn. Mater. **54-57**, 997 (1986).
[18]G. Creuzet, A. Hamzic, and I. A. Campbell, Solid State Commun. **39**, 451 (1981).
[19]S. Senoussi, I. A. Campbell, and A. Fert, Solid State Commun. **21**, 269 (1977).
[20]R. Dupree, R. E. Walstedt, and W. W. Warren, Jr., Phys. Rev. Lett. **38**, 612 (1977).
[21]M. H. Rafailovich, E. Dafni, H.-E. Mahnke, and G. D. Sprouse, Phys. Rev. Lett. **50**, 1001 (1983).
[22]R. Kowallik, H. H. Bertschat, K. Biedermann, H. Haas, W. Müller, B. Spellmeyer, and W.-D. Zeitz, Phys. Rev. Lett. **63**, 434 (1989).
[23]D. Riegel, H. J. Barth, L. Büermann, H. Haas, and Ch. Stenzel, Phys. Rev. Lett. **57**, 388 (1986).
[24]J. W. Loram and K. A. Mirza, J. Phys. F **15**, 2213 (1985).
[25]G. Chouteau, Physica B+C **84B**, 25 (1976); D. Sain and J. S. Kouvel, Phys. Rev. B **17**, 2257 (1978); T. D. Cheung, J. S. Kouvel, and J. W. Garland, *ibid.* **23**, 1245 (1981); T. D. Cheung and J. S. Kouvel, *ibid.* **28**, 3831 (1983).
[26]A. T. Aldred, B. D. Rainford, and M. W. Stringfellow, Phys. Rev. Lett. **24**, 897 (1970).
[27]G. J. Nieuwenhuys, Adv. Phys. **24**, 515 (1975).
[28]P. Raghavan and R. S. Raghavan, Hyperfine Interact. **24-26**, 855 (1985).
[29]H.-E. Mahnke, in *Nuclear Methods in Magnetism,* edited by F. J. Litterst and G. M. Kalvius (Baltzer, Basel, 1989), p. 77.
[30]J. M. Poate and A. G. Cullis, in *Treatise on Materials Science and Technology,* edited by J. K. Hirvonen (Academic, New York, 1980), Vol. 18, p. 85.
[31]D. K. Brice, in *Application of Ion Beams to Materials,* IOP Conf. Ser. No. 28, edited by G. Carter, J. S. Colligon, and W. A. Grant (IOP, London, 1976), p. 334.
[32]H. Bertschat, H. Haas, F. Pleiter, E. Recknagel, E. Schlodder, and B. Spellmeyer, Phys. Rev. B **12**, 1 (1975); R. Butt, H. Haas, T. Butz, W. Mansel, and A. Vasquez, Phys. Lett. **64A**, 309 (1977).
[33]D. A. Micha, Phys. Rev. **156**, 627 (1967).
[34]E. Dafni and G. D. Sprouse, Hyperfine Interact. **4**, 777 (1978).
[35]B. Spellmeyer *et al.* (unpublished).
[36]P. Jarvis, J. Phys. (Paris) Colloq. **45**, C1-803 (1984).
[37]W. N. Lawless, Rev. Sci. Instrum. **42**, 561 (1971).
[38]J. Bleck, R. Michaelsen, W. Ribbe, and W.-D. Zeitz, in *Hyperfine Interaction in Excited Nuclei,* edited by G. Goldring and R. Kalish (Gordon and Breach, New York, 1971).
[39]W. Treutmann, Z. Angew. Phys. **30**, 5 (1970).
[40]G. Chouteau, Ph. D. thesis, University of Grenoble, Grenoble, France, 1973.
[41]G. Chouteau, R. Tournier, and P. Mollard, J. Phys. (Paris) Colloq. **35**, C4-185 (1974).
[42]T. Takahashi and M. Shimizu, J. Phys. Soc. Jpn. **20**, 26 (1965).
[43]A. J. Freeman and R. E. Watson, in *Magnetism,* edited by G. T. Rado and H. Suhl (Academic, New York, 1965), Vol. 2A, p. 167.
[44]H. Kojima, R. S. Tebble, and D. E. G. Williams, Proc. R. Soc. London, Ser. A **260**, 237 (1961).
[45]A. Oswald, R. Zeller, and P. H. Dederichs, Phys. Rev. Lett. **56**, 1419 (1986).
[46]W. D. Zeitz, Ph. D. thesis, Freie Universität Berlin, Berlin, FRG, 1974.
[47]J. W. Loram and K. A. Mirza, J. Phys. F **17**, 1445 (1987).
[48]P. Lederer, in *Magnetism,* edited by S. Foner (Gordon and Breach, New York, 1976).
[49]P. W. Anderson, Phys. Rev. **124**, 41 (1961).
[50]L. L. Hirst, Z. Phys. **241**, 9 (1971).
[51]L. L. Hirst, Z. Phys. **245**, 378 (1971).
[52]P. T. Coleridge, P. Wise, P. H. P. Reinders, and M. Springford, J. Phys. F **16**, 2027 (1986).
[53]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970), p. 462.