HYPERFINE INTERACTIONS OF IMPURITIES IN DEFECT SITES
IN ION-IMPLANTED METALS

(IS20)

G. Weyer

EP Division, CERN, CH-1211 Geneva 23, Switzerland

The lattice location of ion-implanted radioactive isotopes in metals and their interactions with defects in their own radiation damage cascade are of importance for studies of the hyperfine interactions of such probe atoms by nuclear methods. Recent results from Mössbauer and PAC experiments in particular are reviewed. Emphasis is put on lattice site identifications, which can be inferred from measured lattice-dynamical and hyperfine interaction parameters of probe atoms. Some general conclusions on the hyperfine interactions in interstitial- and vacancy-type complexes are drawn.

1. INTRODUCTION

Defect structures created in metals by heavy ion implantation with energies ≥ 10 keV are known to be of rather complex nature in contrast to those resulting from light particle irradiations (e^- , p), where Frenkel pair production prevails under low fluence conditions /1/. This is due to the deposition of large amounts of energy in volumes of atomic dimensions. Elastic collisions of implanted ions with host atoms generate defect cascades of displaced host atoms for an energy transfer $\gg E_d$, where the displacement energy E_d is about $E_d = 10 - 50$ eV in metals. Computer simulations of (sub) cascade evolution and direct experimental observations indicate high concentrations of vacancies (up to $\sim 10\%$) and displaced atoms within the cascade volume /1/. In highly symmetric metals cascade cores are vacancy rich, whereas displaced host atoms (self interstitials) are transported to the periphery. Within about 10^{-12} s relaxation processes in the highly excited cascades (close pair recombination) reduce the defect concentrations and promote defect clustering. Such processes and the formation of clusters in their final configuration (at low temperature) continues during the cooling phase ($\sim 10^{-13}$ s) of the cascades. Subsequently, at elevated sample temperature, where one or several defect species are mobile on a ≥ 10 nm scale by thermally activated

(Presented at the Workshop on On-Line Nuclear Orientation,
Oxford, Aug. 31 - Sept. 4, 1988)

migration, further annealing and clustering of defects occurs. For the fate of the implanted ion, i.e. its final lattice location and incorporation into defect structures, in low temperature implantations the relaxation and cooling phases appear to be most important. This applies a fortiori if the implant is an impurity in the host lattice, which may interact with lattice defects in its immediate surrounding, e.g. trap such defects /2/. This is referred to as athermal trapping in contrast to trapping, which may take place when defects become mobile on a scale of the cascade dimensions at elevated temperature.

Information about the lattice location of the implant and its local configuration on an atomic scale is obtained by various experimental techniques determining the hyperfine interactions of probe atoms or from channeling techniques. To avoid the complexity introduced by the overlap of individual damage cascades from different implanted probes in high-fluence implantations, fluences $\leq 10^{13} \text{ cm}^{-2}$ are necessary. Owing to their superior sensitivity nuclear methods utilizing radioactive implanted probes have been applied in such low-fluence experiments. Notably, Mössbauer spectroscopy (MS) and perturbed angular distribution (PAD) and correlation (PAC) techniques as well as (to a lesser extent) low-temperature nuclear orientation (NO) or NMRON techniques have found widespread applications. For recent reviews of this field see refs. 3-7. Recently, also channeling/blocking measurements of e^- and e^+ emitted from implanted radioactive probes have been employed, which give the lattice location of the probes more directly /8/.

In this paper results mainly from low-fluence investigations of fcc metals by such techniques are presented. The examples given have been selected to illustrate the potential and limitations of the methods rather than to cover all recent progress in the field. In the presentation a sequence has been chosen with respect to a hierarchy of questions, which may be posed:

1. What is the lattice location of the implant at sufficiently low temperature to prevent thermally activated interactions?
 2. What are the interactions of the implant with lattice defects from its own damage cascade - which generally impurity-related defects are formed?
 3. What can be learned about the structure of defects from interpretations of the measured hyperfine interaction and lattice dynamical parameters of the probe atoms?
2. DEFECT CHARACTERIZATION BY BASIC PROBE PARAMETERS ACCESSIBLE TO HYPERFINE INTERACTION TECHNIQUES

By Mössbauer spectroscopy the electric monopole interaction of the probe is determined from the measured isomer shift, which is given by $S = \alpha (\rho_a(0) -$

$\rho_s(0)$). Here ρ_a and ρ_s are the contact electron densities (ced) at the absorber and source nucleus, respectively. The proportionality constant α , which contains the change in mean square nuclear charge radius for the nuclear states involved, has been calibrated to an accuracy of $\sim 10\%$ for many Mössbauer isotopes /9/. For the particular case of ^{119}Sn discussed here, ced values have been calculated for substitutional impurities in metals /10/. Hence from measured changes in the ced for non-substitutional or defect-associated substitutional probes qualitative conclusions on the changes of the electronic configuration of the probe can be drawn.

The electric quadrupole interaction characterized by the interaction frequency $\nu_Q = eQV_{zz}/h$ is determined by MS, PAC and NO techniques. For known quadrupole moments eQ of the nuclear states, the largest component of the electric field gradient (efg) tensor, V_{zz} , is obtained. The magnitude and symmetry properties of the efg give information on the symmetry of the (nearest neighbour) probe surrounding. Progress in theoretical efforts to calculate efgs is reported in this workshop /11/.

The magnetic dipole interaction $E_m = -g \mu_N B$ is determined also by all three techniques. Since g -factors of the nuclear states are generally known with high precision this yields the local magnetic field B at the probe nucleus, which is sensitive also to the local surrounding. Magnetic hyperfine fields in ferromagnetic 3d hosts have been calculated for many substitutional impurities /12,13/.

By MS in addition to the basic hyperfine interaction parameters given above, the mean square vibration amplitude $\langle x^2 \rangle$ of probe atoms is determined from the measured Lamb-Mössbauer factor: $f = \exp(-k^2 \langle x^2 \rangle)$. Here k is the wave vector of the Mössbauer radiation. Parametrized in a Debye model the impurity Debye temperature is determined, which is rigorously defined from the moments of the impurity vibrational frequency spectrum. Force constants characterizing the impurity bonding in the lattice can be obtained from simple model calculations for substitutional impurities /14/. Apart from these basic parameters given above, the time or temperature dependence of such quantities, e.g. relaxation rates of hyperfine interactions, may give information on dynamical processes characterizing the local probe interactions.

Basic parameters for impurity defect complexes have been determined for a variety of interstitial- and vacancy-type complexes in fcc, bcc, and hcp metals (see refs. 3-7, 15). Complexes have been produced by various procedures, some of which allow for an identification of the lattice defect type involved. Uncorrelated production of defects (Frenkel pairs) by e^- -irradiation enables this identification in experiments where complexes with substitutional probes are formed by trapping of long-range migrating lattice defects. It is widely accepted that in fcc metals free migration of self interstitials occurs in annealing stage I (40-100 K), whereas vacancies (and small vacancy clusters) become mobile in stage III (200-400 K). Hence trapping in these different temperature ranges is taken as evidence for the formation of interstitial or vacancy-type complexes, respectively.

Such experiments have been performed with the $^{111}\text{In} \rightarrow ^{111}\text{Cd}$ PAC probe, where interstitial complexes are formed in a few cases, whereas vacancy complexes are formed in many metals/15/. The interpretation of stage III reactions as due to trapping of migrating vacancies or small vacancy clusters is corroborated from results of analogous quenching experiments, whereby supersaturated concentrations of vacancies are obtained. Furthermore, vacancy complexes are also created by neutrino recoil effects in the decay $^{111}\text{Sn} \rightarrow ^{111}\text{In} \rightarrow ^{111}\text{Cd}$, where the recoil energy of $E_R = 29$ eV imparted to the ^{111}In daughter exceeds the displacement energy in some metals/15/. Finally, this interpretation is in accordance with defect-antidefect reaction results, where impurity-vacancy complexes have been annihilated below stage III temperature by reaction with mobile interstitials created in low-temperature irradiations. These studies have resulted in well founded classifications of mono- and divacancy complexes in particular by the magnitude and direction of the efg at the ^{111}Cd probe with respect to axial crystal directions. Selected data from recent compilations are given in Table 1 (refs. 3,4,15). The assignments made for defects formed in ion implantations lean heavily on these systematic data. Trapping of self interstitials in e^- - and n^- - irradiated fcc and bcc metals has been studied by ^{57}Fe MS with radioactive ^{57}Co /15-18/. These results are the basis also for the identification of interstitial defect types in ion implantations as discussed in the following section.

Table 1: Quadrupole interaction frequency ν_Q , asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$ and axial direction $\langle h k l \rangle$ of efgs for ^{111}Cd in mono- and divacancy complexes in fcc metals. The formation temperature after irradiation or quenching is given and production/annihilation type of experiments are indicated.

	Monovacancy complex							Divacancy complex			
	Al	Co	Cu	Pd	Ag	Au	Pt	Al	Cu	Au	Pt
ν_Q (MHz)	66	130	116	87	82	91	103	133	181	101	210
η	0,4	0	0	0	0	0	≤ 0.1	0	0	0	$\leq 0,1$
$\langle h k l \rangle$	110	110	110	110	110	110	-	111	100	100	-
T_{trap} (K)	200	-	230	-	210	220	-	180	200	200	-
quench	x	-	x	-	-	x	-	x	x	-	-
v-recoil	x	-	x	-	x	-	-	x	-	-	-
ion impl.	x	x	x	x	(x)	x	x	x	x	x	x
antidefect. reaction	-	-	x	-	-	x	-	-	x	-	-

3. LOW TEMPERATURE IMPLANTATIONS OF ^{57}Fe AND ^{57}Co INTO ALUMINIUM

Coulomb-excited ^{57}Fe Mössbauer isotopes have been produced with a 130 MeV pulsed Ar beam (pulse length 1 ns, repetition rate 10 MHz) at the VICKSI accelerator of the Hahn-Meitner Institute (Berlin). The recoil energy ($E_R \approx 1$ MeV) of the excited nuclei is sufficient to expel them from an ^{57}Fe target foil and allow for an implantation with a fluence $\leq 10^{10} \text{ cm}^{-2}$ into aluminium foils held at 5-200 K [19]. Time-delayed Mössbauer spectra were measured in between beam bursts by resonance counting techniques [20]. The spectra showed two well known lines attributed to substitutional and interstitial Fe, respectively.

Fig. 1: Line intensities for ^{57}Fe in aluminium versus measuring temperature.

Fig. 2: Model for interstitial Fe in aluminium (defect line in Fig. 1b).

The latter line exhibits an unresolved quadrupole splitting ($E_Q = 0,18 \text{ mm/s}$) and is shifted by $\Delta S = +0,43 \text{ mm/s}$ relative to the substitutional line. The temperature

dependence of the substitutional line intensity is well described by a Debye curve known previously for substitutional Fe as indicated in Fig. 1. This gives evidence that the substitutional Fe fraction (40%) does not change in the investigated temperature interval. The line intensity of the 60% interstitial fraction drops sharply above 40K. This behaviour is the signature of a local cage motion of interstitial Fe. From detailed investigations of the temperature and angular dependence of the line intensity with respect to axial crystal directions when this complex is formed by interstitial trapping in stage I in e^- - and n-irradiated samples, a model for the cage jump motion as shown in Fig. 2 has been developed/16/. The interstitial Fe impurity is displaced slightly from the octahedral interstitial site and performs fast jumps above 40K within the lifetime of the Mössbauer state ($\tau = 140$ ns) between eight equivalent lattice positions. The emission probability of the Mössbauer γ radiation in the fast jump limit is described by:

$f(k) = \left| \frac{1}{N} \sum_N \exp(ikR_N) \right|^2$, where N denotes the number of lattice sites and R_N their position vector. For low defect density (e^- -irradiation) the onset of the cage motion is very sharp (lower curve in Fig. 1b), whereas the motion is hindered in n-irradiated samples (upper curve), presumably due to multiple interstitial trapping. The curve for ion-implanted ^{57}Fe is inbetween these two extreme cases, thus indicating some hindrance in a defect cascade surrounding. The cage motion effect has been observed in other fcc metals/16/ and recently in $\alpha\text{-Zr}$ /21/. In hcp $\alpha\text{-Zr}$ a pronounced well resolved quadrupole splitting ($E_Q = 0,95$ mm/s) for interstitial Fe shows relaxational collapse to about half it's value at the onset of cage motion, thus giving evidence of this effect also in the hyperfine interaction.

It is instructive to compare the results for the on-line ^{57}Fe implantation into aluminium to those obtained by Verbiest and Pattyn/22/ for similar off-line implantation of ^{57}Co ($T_{1/2} = 270$ d) at 4K with an energy of 85 keV to a fluence of $2 \cdot 10^{14} \text{ cm}^{-2}$. Whilst the (slightly) different nature and the lower energy of the implant may be anticipated to be of minor importance for it's fate at the end of the slowing-down process, the overlap of damage cascade volumes for the higher fluence may lead to athermal interactions of the impurity with defects created in the cascades of subsequently implanted impurities. At 4K substitutional Co_s and interstitial Co_i fractions of 53 and 37%, respectively, were found. The higher substitutional fraction may be indicative of a reaction $\text{Co}_i + \text{V} \rightarrow \text{Co}_s$ due to the high vacancy concentration in the (overlapping) cascades. Also, a third line ($\Delta S = + 0,32$ mm/s) was found at 4K, which is attributed to a 10% fraction of Co-vacancy complexes. Furthermore, this fraction increased to 30% upon annealing (30 min) at 180K, where mono- and divacancies are mobile on a > 10 nm scale, whereas the interstitial fraction annealed at this temperature most likely due to annihilation by vacancies: $\text{Co}_i + \text{V} \rightarrow \text{Co}_s$. Since the Debye temperature for the Fe- V_n line is only insignificantly lower than for substitutional Fe presumably mono-or divacancy complexes are formed ($\text{Co}_s\text{-V}_{1,2}$). In contrast to these results, no interactions with migrating defects are expected in the ^{57}Fe on-line implantations as the migration path within the lifetime of the Mössbauer state is too short.

4. IMPLANTATIONS OF ^{119}In and ^{111}In INTO ALUMINIUM

Radioactive ^{119}In ($T_{1/2} = 2$ min) was implanted with an energy of 60 keV and fluences $\leq 10^{12} \text{ cm}^{-2}$ into aluminium single crystals between 15-300 K at the ISOLDE on-line facility at the CERN (Geneva)/23/. Mössbauer spectra were measured for the 24 keV transition of the ^{119}Sn daughter. Below 180 K the spectra show a dominating line from substitutional Sn and a 15% fraction attributed to a defect complex (c.f. Fig. 3). Above 200K a new defect line occurs in the spectra (up to 40%), which is attributed to the formation of a cubic $\text{In}_i\text{-V}_4$ complex, most likely by trapping of mobile multivacancies. In this complex the impurity is proposed to be located on the tetrahedral interstitial site surrounded symmetrically by four vacancies (Fig. 4). The Debye temperature of ^{119}Sn in this complex is lowered considerably (by a factor of 0,7) compared to substitutional Sn and the ced is increased ($\Delta p = 7 \text{ a}_0^{-3}$). The defect anneals at 300K.

Fig. 3: Substitutional (upper curve) and defect fractions (lower curve) for ^{119}In in aluminium as a function of implantation/annealing temperature.

Fig. 4: Model of the relaxed In-trivacancy complex (40% defect fraction of Fig. 3, impurity-open circle, vacancies-open squares).

PAC results /24/ on ^{111}Cd for implanted ^{111}In ($10^{13}\text{-}10^{14} \text{ cm}^{-2}$, 110 keV) give evidence of the presence of two different non-cubic defects below 200K with quadrupole interaction frequencies of $\nu_Q = 68$ and 131 MHz, respectively. From a recent discussion of other ^{111}In PAC data/25/ these may be attributed to the athermal formation of In-V and $\text{In}_i\text{-V}_3$ complexes, respectively (c.f. Table 1). The latter structure is a relaxed divacancy complex (Fig. 5), where the impurity is displaced in the $\langle 111 \rangle$ direction surrounded by three vacancies, which resembles the $\text{Sn}_i\text{-V}_4$ configuration. Fractions of 5-10% of these defects are compatible with

the MS results. However, owing to a larger quadrupole moment of the ^{111}Cd PAC state and to higher resolution as compared to ^{119}Sn MS, the PAC technique is more sensitive to an efg at the impurity. On the other hand, cubic defect configurations are invisible to PAC techniques (in non-magnetic hosts) due to the absence of an efg. Hence the assignment of a 40% $\text{In}_i\text{-V}_4$ complex fraction from MS in the 200-300K interval is consistent with the absence of any defect signal in the PAC spectra in this interval. Above 300K a new defect ($\nu = 49$ MHz) with $\langle 111 \rangle$ efg direction occurs in the PAC spectra, which is attributed to the formation of a faulted loop/24/.

The results obtained for the formation and accretion of In-V_n complexes in aluminium appear typical also for other fcc metals. Generally by ion implantation fractions of 5-15% of In-V and In-V_2 complexes are formed athermally below stage III temperature (c.f. Table 1). Upon annealing in stage III the mobility of di- and/or trivacancies leads to the formation of larger vacancy complexes, in particular the $\text{In}_i\text{-V}_4$ complex is formed in fractions of 20-60%. The Mössbauer parameters of such complexes (from ref. 26) are listed in Table 2, where results discussed in the following sections have been included. This defect appears to be

Table 2: ^{119}Sn Mossbauer parameters for the $\text{Sn}_i\text{-V}_4$ complex formed with ^{119}In or ^{119}Sb precursors. S_s is given relative to CaSnO_3 , S_i and θ_i relative to substitutional Sn.

Host	S_s (mm/s)	θ_s (K)	$S_i - S_s$ (mm/s)	θ_i / θ_s	T_{trap} (K)	P_{max} (%)
Al	2.27	170	0.48	0.68	200	40
Ni	1.55	310	0.34	0.65	370	20
Co	1.68	295	0.33	0.8	350	15
Cu	1.74	210	0.42	0.88	260	25
Pt	1.25	250	0.54	0.80	400	60

the most abundant complex formed in stage III in ion implanted fcc metals. It has been considered as a possible nucleation center for the growth of stacking fault tetrahedra/26/. It is interesting to note that the ^{111}In PAC data (Table 1) indicate the athermal formation of an unrelaxed monovacancy complex, In-V_1 (with the possible exception of Al) from the efg symmetry, where the vacancy is on the nearest neighbour site to the substitutional probe (Fig. 5). Two different divacancy complex configurations are proposed as shown in Fig. 5: An unrelaxed configuration with two nearest neighbour vacancies, $\text{In}_s\text{-V}_2$, for Cu and Au and the relaxed configuration, $\text{In}_i\text{-V}_3$, which is proposed for Al and Ni (c.f. sect. 5).

Fig. 5: Models of In-mono- and -divacancy complexes in fcc metals.

In Al and Cu detailed models of further vacancy accretion to such complexes have been derived/25/ which lead to their transformation to the In_i-V₄ complex. These are in overall agreement with the MS results for Al (given above) and Cu/27/. In Ni and Co, on the other hand, at least the In-V complex is not involved in the formation of the In_i-V₄ complex and evidence for a direct trapping of mobile trivacancies has been found (see following section and ref. 28). The large fractions of In_i-V₄ complexes suggest that this direct trapping reaction is also of importance for the other ion implanted fcc metals. Furthermore, it emerges from Table 1 that divacancies become mobile at slightly lower temperature than monovacancies. This is also indicated in some cases for trivacancies (see below). The ¹¹⁹Sn MS parameters for the Sn_i-V₄ complex may be understood at least qualitatively. In this complex the impurity is surrounded by 12 nearest neighbour host atoms as on substitutional sites, however, their distance is larger by 17% assuming no relaxation. Thus the impurity may be considered as localized in a locally strongly dilated lattice surrounding. From the measured pressure dependence of the isomer shift for substitutional Sn in other fcc metals an increase in ced is expected for a dilated lattice, which is consistent with the order of magnitude of the observed increase in ced for the In_i-V₄ complex by $\Delta\rho = 5-8 \text{ a}_0^{-3} /6/$. Also the pronounced increase in $\langle x^2 \rangle$ for Sn in this complex is in accordance with intuitive expectations.

5. IMPLANTATIONS OF ¹¹⁹Xe, ¹¹⁹In and ¹¹¹In INTO FERROMAGNETIC 3d METALS

Radioactive ¹¹⁹In and ¹¹⁹Xe were implanted at 297K with an energy of 60 keV into fcc cobalt and nickel to fluences $\leq 10^{13} \text{ cm}^{-2}$ at the ISOLDE facility/29,30/. The trapping of lattice defects from the radiation damage cascade was followed as a function of isochronal annealing temperature. For the ¹¹⁹Xe-implanted samples annealing was performed after the nuclear decay to ¹¹⁹Sb ($T_{1/2} = 38 \text{ h}$) had occurred, hence the trapping behaviour of In and Sb, respectively, is probed by MS with the common ¹¹⁹Sn daughter. Various different defect complexes were identified in the spectra, which were assigned to (multi)vacancy complexes; the parameters are listed in Table 3. Recently, very similar results have been

reported by the Groningen group/7/ for ^{119}Sb -implanted nickel, who also found some of the defect complexes to be formed upon deformation of nickel. The structural assignments for the different vacancy complexes lean heavily on the identification of the most prominent defect with the largest magnetic hyperfine splitting as the relaxed trivacancy complex $\text{In}_i\text{-V}_4$. This identification is strongly supported from channeling experiments/29/ on emitted e^- and e^+ from implanted radioactive In isotopes under similar conditions as for the MS experiments. These experiments prove that about 30% of the substitutionally-implanted In probes move to the tetrahedral interstitial site upon annealing to ~ 400 K. Above 650 K only substitutional In is found. This behaviour is in perfect agreement with the annealing behaviour in the MS spectra. Furthermore, the same annealing behaviour was observed in previous ^{111}Cd PAC experiments for implanted ^{111}In , which led to the first proposal of a cubic $\text{In}_i\text{-V}_4$ structure to this complex in particular based upon the absence of any quadrupole interaction/31/. Also the vacancy nature of this defect is corroborated from PAC and channeling results on irradiated samples/28,32/. Evidence for the formation of smaller fractions of different vacancy complexes was also obtained in the PAC experiments, although these could not be well characterized by their hyperfine interaction parameters in general. Analogously, in the MS after implantation weaker components are indicated as listed in Table 1. Clear evidence for most of these components is obtained from the results of ^{119}Xe implantations, where (except for the $\text{Sn}_i\text{-V}_4$ complex) larger defect fractions are found.

Table 3: MS parameters for $^{119}\text{Sn-V}_n$ complexes in fcc Co and Ni.
The internal magnetic field B is given at 77 K (without correction for the Lorenz field), S is relative to CaSnO_3 .

Host	S (mm/s)	B (T)	θ (K)	assignment
Ni	1.55	+ 2.0	308	subst. Sn
	1.72	+ 7.7	223	$\text{Sn} - \text{V}$
	1.73	+ 9.1	230	$\text{Sn}_i\text{-V}_6, \text{Sn}_i\text{-V}_{10}$
	1.83	+14.4	240	$\text{Sn}_i\text{-V}_3$
	1.89	+16.5	214	$\text{Sn}_i\text{-V}_4$
Co	1.68	- 2.4	295	subst. Sn
	1.87	17.2	-	$\text{Sn} - \text{V}_n ?$
	2.0	30.	-	$\text{Sn}_i\text{-V}_3 ?$
	2.01	+36.1	241	$\text{Sn}_i\text{-V}_4$

This is attributed to recoil effects in the decay sequence from ^{119}Xe to ^{119}Sb . The structural assignments made for the components are mainly based on the annealing behaviour as compared to the $\text{Sn}_i\text{-V}_4$ complex and the values of the hyperfine interaction and θ parameters.

A detailed discussion of the site assignments given in Table 3 is beyond the scope of this paper, however, the prominent features of the hyperfine interactions found for the vacancy complexes will be pointed out. The magnetic hyperfine fields of substitutional sp impurities in ferromagnetic 3d hosts are theoretically well understood/12,13/. The B_{hf} values exhibit a similar systematic behaviour in every sp period. Large negative values are found in the beginning of a period. These are attributed to a predominant hybridisation of the impurity sp valence electrons with minority-spin d-electrons of the hosts, giving rise to negative fields by the Fermi-contact interaction. When going through the period new states related to majority-spin d-electrons become more important until they dominate at the end of the period, where large positive values are found. Sn impurities in the middle of the 5sp period have the lowest B_{hf} values in all 3d hosts due to an almost complete cancellation of (large) negative and positive contributions. Therefore B_{hf} for this impurity should be sensitive to minute changes in its local

Fig. 6: Changes in isomer shifts and magnetic hyperfine fields for Sn-V_n complexes relative to substitutional Sn. The B_{hf} scales are adjusted in the ratios of the magnetic moments (spin fractions) of the hosts.

surroundings disturbing this delicate balance. From inspection of Table 3 it emerges that the fields increase in orderly sequence for mono-, di-, and trivacancy complexes, having proposed structures of Sn-V , $\text{Sn}_i\text{-V}_3$ and $\text{Sn}_i\text{-V}_4$, respectively. The field decreases again for the complex assigned to $\text{Sn}_i\text{-V}_6$ or $\text{Sn}_i\text{-V}_{10}$ where Sn is either located on the octahedral interstitial site surrounded symmetrically by six vacancies or on the tetrahedral interstitial site in a relaxed structure as discussed below. The increase in B_{hf} for all vacancy complexes is correlated to an increase in isomer shift as shown for Ni and Co in Fig. 6. The correlation is very similar in both hosts when scaled with the (spin fractions) of the magnetic moments of the host atoms as can be seen in Fig. 6 from the lines connecting the most accurately determined values for substitutional Sn and the $\text{Sn}_i\text{-V}_4$ complex. Results from ^{119}In implantations into Fe are also included/33-35/, where mono- and divacancy complexes are proposed to be formed athermally and/or by trapping in stage III (200K).

Since the isomer shift is proportional to the total s-electron density $|\psi(0)|^2$ (neglecting p-electron contributions) and B_{hf} is proportional to the difference in spin-up and spin-down s-electron density, $(|\psi^\uparrow(0)|^2 - |\psi^\downarrow(0)|^2)$, this correlation suggests that the increase in B_{hf} is due to an increase in ced of prevailing spin-up character. This is in accordance with the general results of the model calculations/12,13/ and might be expected also from the measured pressure dependencies of S and B_{hf} for substitutional Sn/35/. These results allow for some qualitative conclusions on the local density of states for the Sn impurity in the 3d hosts as discussed elsewhere/35/, however, obviously detailed model calculations are required to arrive at a more profound understanding of the changes of S and B_{hf} for Sn-V_n complexes. The rather varied nature of defect complexes revealed by the magnetic splitting in Ni may conceivably be present in non-magnetic hosts also, where they cannot be resolved, however, on the basis of the measured S value alone. In fcc Co indications for several more complexes than given in Table 3 were found/30,34/ but these have been omitted since they were not well established. More detailed information on vacancy complexes found in ion-implanted Co has been obtained from a $^{111}\text{In} - ^{111}\text{Cd}$ PAC study/36,38/ utilizing the IONAS facility at Göttingen University to implant ^{111}In with an energy of 250 keV to fluences of 10^{13} - 10^{14} cm^{-2} into fcc Co between 100-300 K. Fractions of 3% of $\text{In}_s\text{-V}$ complexes were formed athermally below stage III temperature (340-380K) and remained stable up to 400K, whereas the $\text{In}_i\text{-V}_4$ complex was formed in fractions of up to 15% by trapping of mobile di-or trivacancies at 320K. This complex is transformed into a larger $\text{In}_i\text{-V}_{10}$ complex at 580K by trapping of a trivacancy released from larger clusters. This is proposed to lead to a relaxation of three host atoms into tetrahedral interstitial sites as shown in Fig. 7.

$\text{In}_i - \text{V}_{10}$

Fig. 7: Model for the relaxed In-hexavacancy complex

From a detailed annealing model/38/ an unobserved In-V_2 complex is predicted to be formed at 320K. Hence di- and trivacancy mobility is indicated at slightly lower temperature than mobility of monovacancies. The determined parameters are gathered in Table 4. The magnetic hyperfine field increases between the Cd-V and $\text{Cd}_i\text{-V}_4$ complexes and decreases again for the $\text{In}_i\text{-V}_{10}$ complex as for Sn complexes in Ni.

Table 4: ^{111}Cd PAC parameters for vacancy complexes in fcc cobalt.
The internal magnetic field B is given at 20 K.

B(T)	ν_Q (MHz)	$\langle hkl \rangle$	T_{trap} (K)	assignment
-24.1	-	-	-	subst. Cd
21	138	$\langle 110 \rangle$	atherm.	Cd - V
-18.3	-	-	320	$\text{Cd}_i - \text{V}_4$
20	66	$\langle 111 \rangle$	550	$\text{Cd}_i - \text{V}_{10}$

The identification of an $\text{In}_s\text{-V}$ complex in this study is strongly supported from the resolved combined magnetic dipole and electric quadrupole interaction, which yields an efg value and symmetry that falls in line with the results for $\text{In}_s\text{-V}$ complexes in non-magnetic fcc metals (c.f. Table 1). The assignment of an $\text{In}_i\text{-V}_{10}$ configuration to the high-temperature complex is corroborated by the smaller efg in $\langle 111 \rangle$ direction, which excludes a symmetric configuration. The analogous annealing behaviour and ordering of B_{hf} values for Cd in vacancy complexes in fcc Co and for Sn in Ni therefore also favours this configuration for the complex formed with Sb in nickel at high temperature/7,28-30/. Fig. 8 displays the

magnetic hyperfine fields/39/ for substitutional 5sp impurities in Ni, Co and Fe together with the values for Cd and Sn in vacancy complexes. The B_{hf} scales have been adjusted in the ratios of (the spin fraction of) the magnetic moments of the host atoms. Co values for the fcc phase are displayed where available.

Fig. 8: Magnetic hyperfine fields of 5 sp impurities on substitutional (filled circles) sites and in vacancy complexes (open circles) in 3d ferromagnetic hosts.

Arrows beside of substitutional data points indicate magnitude and sign of the measured pressure dependence of B_{hf} on a relative scale. A smooth curve has been drawn through the substitutional data points to emphasize the similar systematic trend. The values for the Imp_i-V_4 complexes are connected for the same reason. The latter have been calculated recently in a semiempirical approach based on the substitutional B_{hf} values and their pressure dependence/36/, which models

the defect structure as a local lattice dilatation. The values for both impurities are reproduced reasonably well in both hosts. Thus the positive sign of the changes in B_{hf} and their order of magnitude may be understood within this model. According to these considerations for the smaller vacancy complexes smaller changes should result as is observed experimentally. The smaller values of B_{hf} changes for the Imp_i-V_{10} complex as compared to the Imp_i-V_4 complex may conceivably result from the relaxation in the configuration of the host atoms, which are displaced closer to the probe atoms (c.f. Figs. 4 and 7). Although the experimental results for Sn and Cd can be qualitatively accounted for within this model, an increase in numerical values of the negative and positive values of B_{hf} for Cd and I in Fe, respectively, would be expected for (simple) vacancy complexes from the pressure dependence of B_{hf} . No values have so far been reported for Cd, however, for I an approximately 10% decrease has been found by NMRON for a defect attributed to I_s-V_1 /40/. Also for Fe probes implanted into Fe a reduction (10%) in the magnetic hyperfine field for vacancy associated probes is found/41/, whereas from the simple lattice dilatation model on the basis of the pressure dependence of B_{hf} /42/ an increase would be expected. Presumably, the "magnetic vacancy" character of a lattice vacancy is of primary importance in this pure case. However, it appears conceivable that for sp impurities, where the magnetic hyperfine field stems from the Fermi contact interaction of the valence electrons, the changes in (spin-polarized) electron density resulting from the formation of vacancy complexes as compared to substitutional probes may be approximated by the semiempirical lattice dilatation model. The importance of minute details in the electronic configuration of the impurity is probably also the origin of the observed pronounced differences in the temperature dependencies of the magnetic hyperfine fields for Cd and Sn in fcc cobalt. The temperature dependence of B_{hf} for substitutional Cd shows "normal" behaviour, i.e. follows closely the temperature dependence of the host magnetisation/36/, whereas that for substitutional Sn is highly anomalous/43,44/. Here a change in sign of B_{hf} occurs at $T \sim 700$ K, corresponding to $T \sim 0,5T_c$, where T_c is the Curie temperature. In contrast, the temperature dependence of B_{hf} for the Cd_i-V_4 complex drops much below the magnetisation curve below $T < 0,3 T_c$ /36/, whereas no measurable deviation is observed for Sn in the Sn_i-V_4 complex /44/.

8. CONCLUSIONS

MS and PAC techniques utilizing radioactive probes have proved to be sufficiently sensitive to allow investigations of the microscopic nature of point defects and defect complexes in ion implanted metals. The resolution in hyperfine interactions is in many cases sufficient to distinguish differences in the structures on (at least) a nearest neighbour scale, whereas its limitations prevent an overwhelming complexity in the spectra deriving from the more distant defect cascade surrounding. It is remarkable that the same defect complex types are

formed with a particular impurity as discussed for fcc metals in ion implantation, irradiation, quenching and deformation experiments. From the comparison of different probes under comparable conditions it is evident that impurity-specific complexes with lattice defects are formed, a fact which has to be taken carefully into account in the interpretation of the results with respect to lattice defects produced in ion implantations. Clearly, to arrive at a comprehensive understanding of the defect types in damage cascades complementary methods have to be applied. The examples of impurity defect complexes discussed in this paper appear to be of general nature. Interstitial type complexes tend to be formed for the small probes (Fe, Co) in fcc, (bcc), and hcp metals, whereas vacancy complexes prevail for larger impurities (5sp elements). Such complexes are well characterized by the impurity parameters accessible to nuclear hyperfine interaction techniques. From the wealth of systematic data for such complexes, which has been gathered in recent years, a classification scheme for the different defect types is beginning to emerge and detailed models for the athermal defect formation with impurities as well as further defect accretion and trapping in annealed samples and their annihilation kinetics have been proposed. The extreme sensitivity of the magnetic hyperfine field of some probe elements makes further studies in ferromagnetic hosts look particularly rewarding. Since MS and PAC techniques are restricted to a small number of suitable impurity probes the application of alternative techniques with a wider choice of probes, e.g. NO and NMRON or e^- and e^+ channeling/blocking techniques, could give valuable new information. Also the combination of different techniques and different probe elements having different sensitivity for various impurity parameters appears to have considerable potential to gain more detailed insight into the kinetics of defect reactions and the nature of the defects formed.

Concerning the state of a profound understanding of the hyperfine interaction and lattice dynamical impurity parameters, promising results have been reported for substitutional and interstitial probes, however, calculations of these quantities for impurity-defect complexes are scarce. The semiempirical classification schemes, which have been achieved based on the efg, B_{hf} , S and θ values for impurities in defect complexes, might stimulate further theoretical efforts.

It is a pleasure to acknowledge collaborations and stimulating discussions with many colleagues from Aarhus, Göttingen, Groningen and Konstanz Universities, the Hahn-Meitner Institute in Berlin, and the ISOLDE collaboration at CERN, Geneva.

REFERENCES

- /1/ R.S. Averback and D.N. Seidmann, *Mat. Sci. Forum* 15-18 (1987) 963.
- /2/ O. Meyer and A. Turos, *Nucl. Instr. Meth.* 19/20 (1987) 136.
- /3/ F. Pleiter and C. Hohenemser, *Phys. Rev.* B25 (1982) 106.
- /4/ E. Recknagel, G. Schatz and Th. Wichert in: *Hyperfine Interactions of Radioactive Nuclei*, ed. J. Christiansen, *Topics in Current Physics*, Vol. 31 (Springer, Berlin, 1983), p. 133.
- /5/ L. Niesen, *Hyp. Int.* 24 (1985) 1035.
- /6/ G. Weyer, *Hyp. Int.* 27 (1986) 249.
- /7/ H. de Waard, *Hyp. Int.* 40 (1988) 31.
- /8/ H. Hofsäss, G. Lindner, S. Winter, B. Besold, E. Recknagel and G. Weyer, *Nucl. Instr. Meth.* B13 (1986) 71.
- /9/ G.K. Shenoy and F.E. Wagner: *Mössbauer Isomer Shifts* (North Holland, Amsterdam, 1978).
- /10/ A. Svane, *Phys. Rev. Lett.* 60 (1988) 2693.
- /11/ T.P. Das, these proceedings.
- /12/ M. Akai, H. Akai and J. Kanamori, *J. Phys. Soc. Jap.* 54 (1985) 4246 and 4257.
- /13/ N. Stefanou, H. Akai, R. Zeller and P.H. Dederichs, *Phys. Rev.* B35 (1987) 3271.
- /14/ H. Andreasen, S. Damgaard, J.W. Petersen and G. Weyer, *J. Phys.* F13 (1983) 2077.
- /15/ R. Sielemann, *Mat. Sci. Forum* 15-18 (1987) 25.
- /16/ G. Vogl, *phys. stat. sol. (b)* 144 (1987) 259.
- /17/ W. Mansel, J. Marangos and D. Wahl, *J. Nucl. Mat.* 108 + 109 (1982) 137.
- /18/ J. Marangos, W. Mansel and D. Wahl, *Mat. Sci. Forum* 15-18 (1987) 225.
- /19/ M. Menningen, R. Sielemann, G. Vogl, Y. Yoshida, K. Bonde Nielsen and G. Weyer, *Europhys. Lett.* 3 (1987) 927.
- /20/ G. Weyer, *Nucl. Instr. Meth.* 186 (1981) 201.
- /21/ Y. Yoshida, M. Menningen, R. Sielemann, G. Vogl, G. Weyer and K. Schröder, *Phys. Rev. Lett.* 61 (1988) 195.
- /22/ E. Verbiest and H. Pattyn, *Phys. Rev.* B25 (1982) 5097.
- /23/ F.T. Pedersen, H. Grann and G. Weyer, *Hyp. Int.* 29 (1986) 1241.
- /24/ F. Pleiter and G.K. Prasad, *Hyp. Int.* 20 (1981) 221.
- /25/ Th. Wichert, *Mat. Sci. Forum* 15-18 (1987) 829.
- /26/ G. Lindner and G. Weyer, *Mat. Sci. Forum* 15-18 (1987) 569.
- /27/ H. Andreasen, S. Damgaard, J.W. Petersen and G. Weyer, *Hyp. Int.* 15-16 (1983) 289.
- /28/ C. Allard, G.S. Collins and C. Hohenemser, *Phys. Rev.* B32 (1985) 4839.
- /29/ B. Besold, E. Danielsen, H. Hofsäss, G. Lindner, J.W. Petersen, E. Recknagel, M. Sondergaard, G. Weyer and S. Winter, *Mat. Sci. Forum* 15-18 (1987) 665 and to be published.

- /30/ E. Danielsen, K.B. Nielsen, J.W. Petersen, N. Sondergaard and G. Weyer, Mat. Sci. Forum 15-18 (1987) 669.
- /31/ C. Hohenemser, A. Arends, H. de Waard, H.G. Devare and F. Pleiter, Hyp. Int. 3 (1977) 297.
- /32/ M. Vos, D.O. Boerma and F. Pleiter, Nucl. Instr. Meth. B15 (1986) 333.
- /33/ G. Weyer, F.T. Pedersen and H. Grann, Nucl. Instr. Meth. B7/8 (1985) 103.
- /34/ K. Bonde Nielsen, E. Danielsen, J.W. Petersen, M. Sondergaard and G. Weyer, Hyp. Int. 35 (1987) 643.
- /35/ G. Weyer, Proc. Int. Conf. on Nuclear Methods in Magnetism, München, 1988, to be publ. in Hyp. Int.
- /36/ F. Raether, G. Weyer, K.P. Lieb and J. Chevallier, Phys. Lett. A131 (1988) 471.
- /37/ F. Raether, D. Wiarda, K.P. Lieb, J. Chevallier and G. Weyer, Z. Phys. in press.
- /38/ D. Wiarda, F. Raether, K.P. Lieb, J. Chevallier and G. Weyer, Proc. Int. Conf. on Nuclear Methods in Magnetism, München, 1988, to be publ. in Hyp. Int.
- /39/ G.N. Rao, Hyp. Int. 24-26 (1985) 1119.
- /40/ D. Visser, L. Niesen, H. Postma and H. de Waard, Phys. Rev. Lett. 41 (1978) 882.
- /41/ H.E. Mahnke, Proc. Int. Conf. on Nuclear Methods in Magnetism, München, 1988, to be publ. in Hyp. Int.
- /42/ G.B. Benedek in "Solids under Pressure", eds. W. Paul and D.M. Warschauer (McGraw Hill, New York, 1961), p. 251.
- /43/ M. Senba, P. Raghavan, W. Semmler, R.S. Raghavan, Hyp. Int. 9 (1981) 453.
- /44/ M. Sondergaard, Thesis, Aarhus University, 1988.