PHYSICAL REVIEW B VOLUME 25, NUMBER 8 15 APRIL 1982

Free migration of vacancies in niobium at 250 K

R. Sielemann, H. Metzner, R. Butt, S. Klaumünzer, H. Haas, and G. Vogl
Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Kern- und Strahlenphysik,
and Freie Universität Berlin, Fachbereich Physik, D-1000 Berlin, West Germany

(Received 1 February 1982)

Annealing of defects in high-purity niobium after low-temperature irradiation is investigated using perturbed angular correlation of γ rays from the radioactive probes ^{100}Pd and ^{111}In which are deeply implanted by heavy-ion-induced nuclear reactions. The trapping behavior of the two different probes discriminates between interstitials and vacancies. When the data are combined with defect-orientation measurements in a single crystal we conclude that single vacancies are migrating freely at 250 K.

Results on the location of the stage of free-vacancy migration in the refractory bcc metals, in particular for the group-V transition metals vanadium, niobium, and tantalum, have been extremely difficult to obtain. Where data exist, they are very contradictory. This is primarily because of the strong tendency of these metals to take up C, N, O, and H, masking intrinsic properties. Also the uncommon intrinsic properties themselves hamper interpretation of experimental results along established lines in analogy to fcc metals. In Nb, positron annihilation experiments point to vacancy migration temperatures around 550 K,[1] whereas from recent resistivity measurements after electron irradiation the migration of an intrinsic point defect is suggested for either 250 or 350 K. In this case, however, no assignment to a certain defect type is made.[2] Similar contradictory results exist for V and Ta.

Hyperfine-interaction techniques like Mössbauer effect and perturbed angular correlation (PAC) recently have contributed strongly to the interpretation of intrinsic recovery stages in fcc metals.[3] So far, however, the difficulty of a clean doping of the highly-impurity-sensitive group-V transition metals with radioactive probes by chemical methods or low-energy ion implantation has severely hampered their investigation.

Here we report on an investigation of high-purity Nb by the PAC method using a novel doping technique via heavy-ion-induced nuclear reactions. This turned out to have a series of ideal features for our purpose: (i) Heavy-ion beams produce the probes deep (1–30 μm) in the bulk material at very low concentration (< 0.1 at.ppm), preserving the high purity of the starting material, so that frequencies appearing in the PAC spectra can be assigned to intrinsic defects trapped at the probe. The primary beam either passes through the target or is stopped far away from the produced activity. (ii) The deep implantation allows complete annealing at temperatures above 2000 K in UHV with only moderate loss of radioactivity. This allows a controlled defect production of the doped samples by electron irradiation, which is required for clearcut results on the question of *long-range* defect migration and for the production of simple defects. (iii) Various PAC probes can be excited in Nb which are difficult to apply otherwise and therefore have not been used so far in this research field (e.g., ^{100}Pd).

In our experiment beams of ^{12}C and ^{22}Ne at about 100 MeV from the VICKSI accelerator were used to produce the two radioactive nuclear probes ^{100}Pd and ^{111}In via the reactions $^{93}\mathrm{Nb}(^{12}\mathrm{C},5n)^{100}\mathrm{Ag}\xrightarrow{\beta}{}^{100}\mathrm{Pd}$ and $^{93}\mathrm{Nb}(^{22}\mathrm{Ne},4n)^{111}\mathrm{Sb}\xrightarrow{\beta}{}^{111}\mathrm{Sn}\xrightarrow{\beta}{}^{111}\mathrm{In}$ in Nb.[4] It is essential to this experiment that Pd and In trap different types of lattice defects. From comparison of the trapping and detrapping processes at the different probes, from electron irradiation results, and from measurements in a single crystal we shall conclude that single vacancies undergo long-range migration as low as 250 K. Part of the frequency spectrum we observe at the In probe was also obtained by Vianden and Winand[5] after low-energy implantation, but they cannot contribute to the vacancy migration problem because of assignment difficulties and an irradiation temperature above stage III.

In cubic nonmagnetic materials the trapping of lattice defects at a probe reflects itself in the appearance of a modulation pattern in the PAC spectra. This is because of the quadrupole interaction of the probe's nuclear quadrupole moment Q with the electric field gradient (EFG) eq produced by the defect. In our experiment two nuclear probes are used: ^{111}In ($T_{1/2}=2.8$ d) where the quadrupole interaction frequency ν_Q^{In} is measured on the daughter nucleus $^{111}\mathrm{Cd}(I=\frac{5}{2},\ T_{1/2}=84\ \mathrm{ns},\ Q=0.8\ \mathrm{b})$ and $^{100}\mathrm{Pd}(T_{1/2}=3.8\ \mathrm{d})$, the interaction frequency ν_Q^{Pd} being measured on $^{100}\mathrm{Rh}(I=2,\ T_{1/2}=216\ \mathrm{ns},$ $Q=0.08\ \mathrm{b})$. The quadrupole interaction is described by the interaction frequency $\nu_Q=e^2Qq/h$, the asymmetry parameter η of the EFG tensor, and amplitudes s_n, weighting the frequencies contributing to the experimentally observed spin precession pattern.[6]

In the first part of the experiment 30-μm-thick Nb foils (resistivity ratio 3000–5000) were bombarded with ^{12}C and ^{22}Ne to produce the radioactive probes. The foils were mounted on a copper holder cooled with liquid He, resulting in target temperatures of 30 ± 10 K. This doping simultaneously created lattice defects which were studied in subsequent isochronal annealing experiments. After each temperature step (10 min) a PAC spectrum was measured at 10 K.

The following results are obtained:

(i) ^{100}Pd. Directly after irradiation the PAC spectra show a clear modulation pattern indicating trapping of defects in well-defined configurations during the irradiation. The quadrupole coupling constants extracted from the data are $\nu_{Q1}^{\mathrm{Pd}}=42(2)$ MHz ($\eta_1^{\mathrm{Pd}}=0$) and $\nu_{Q2}^{\mathrm{Pd}}=33(2)$ MHz ($\eta_2^{\mathrm{Pd}}=1$). Both defect configurations are produced at fractions of about $f_i^{\mathrm{Pd}}=10\%$ of the total probe atoms. They are stable up to annealing temperatures around 100 K and then rapidly disappear.

(ii) ^{111}In. In sharp contrast the spectra for this probe do not show a unique modulation up to 200 K; only a damping due to a broad frequency distribution is visible. This is attributed to distant lattice damage. Above 200 K trapping occurs: Two defect-induced frequencies show up with $\nu_{Q1}^{\mathrm{In}}=87(1)$ MHz ($\eta_1^{\mathrm{In}}=0$) and $\nu_{Q2}^{\mathrm{In}}=105(2)$ MHz ($\eta_2^{\mathrm{In}}=0.65$). Above 250 K a third defect configuration is produced with $\nu_{Q3}^{\mathrm{In}}=177(2)$ MHz ($\eta_3^{\mathrm{In}}=0$), which in contrast to the others has a large frequency spread. Figure 1 shows PAC spectra measured with ^{100}Pd (top) and with ^{111}In (middle) after heavy-ion irradiation. Figure 2 displays the fractions of ^{100}Pd and ^{111}In probes with trapped defects as a function of annealing temperature.

In the second part of our experiment the foils were annealed at 2100 K after doping with ^{111}In by the heavy-ion reaction. Subsequent PAC measurements showed a cubic environment. The foils were then irradiated with 2.5-MeV electrons at 77 K to a total dose of 1.8×10^{18} e^-/cm^2. Trapping of defects starts in the same temperature region as observed after heavy-ion irradiation, and the same defects, characterized by ν_{Q1}^{In} and ν_{Q2}^{In} and the respective asymmetry parameters η_1^{In} and η_2^{In} are obtained. The fractions f_1^{In} and f_2^{In} are somewhat lower compared with heavy-ion irradiation. There appears, however, no component with frequency ν_{Q3}^{In}, in contrast to the result observed after heavy-ion irradiation. Figure 1 (bottom) shows a PAC spectrum measured with ^{111}In after electron irradiation which is to be compared with the spectrum obtained after heavy-ion irradiation (middle), both at $T_A=250$ K.

In the third part of the experiment a 1-mm-thick Nb single crystal (resistivity ratio: 3800) was doped with ^{111}In at 77 K as described before and then

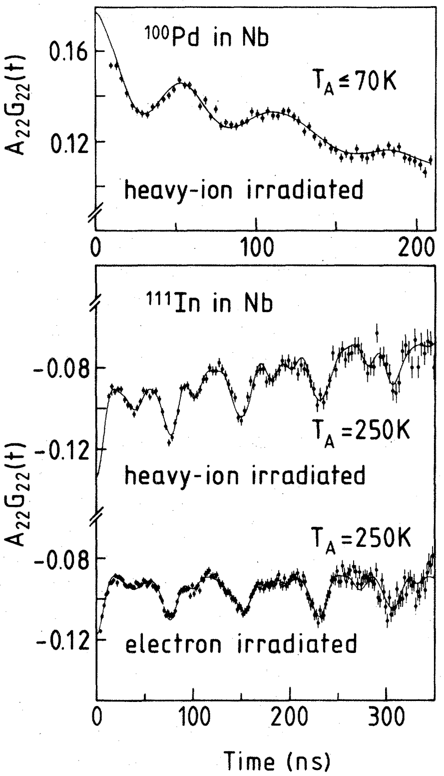

FIG. 1. Time-differential PAC spectra of ^{100}Pd in Nb (top) and ^{111}In in Nb (middle) after heavy-ion irradiation and ^{111}In in Nb after electron irradiation (bottom) at annealing temperatures T_A.

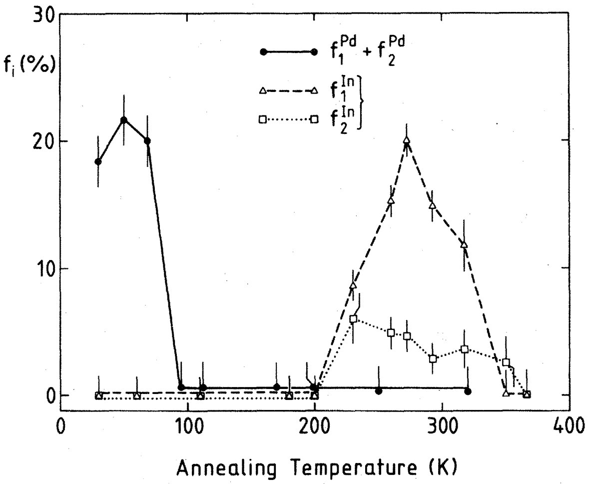

FIG. 2. Fractions f_i of ^{100}Pd and ^{111}In probe atoms which have trapped defects of type ν_{Qi} after heavy-ion irradiation at 30 K as a function of annealing temperature T_A. Fraction f_3^{In} is omitted for clarity.

directly annealed at 250 K, the temperature of maximum trapping for the defects ν_{Q1}^{In} and ν_{Q2}^{In}. Three individual PAC measurements were performed with the detectors pointing either into ⟨100⟩, ⟨110⟩, or ⟨111⟩ directions of the crystal. The data were Fourier analyzed to obtain effective amplitudes s_n,[6] which yield in an unambiguous way the orientation of the EFG. Table I shows the result of a measurement with the counters in the ⟨111⟩ directions. Theoretical predictions for the s_n are given for the different possible directions of the z axis of the EFG. Our very clear cut data give the orientation of the EFG connected with ν_{Q1}^{In} uniquely as ⟨111⟩. The data with the counters in ⟨100⟩ and ⟨110⟩ directions confirm that result. The orientation of the defect ν_{Q2}^{In} cannot be obtained from our data since the nonzero asymmetry parameter $\eta_2^{\mathrm{In}} = 0.65$ in this case very much reduces the sensitivity of the amplitudes s_n to different orientations. No effort was made to measure the direction of the EFG connected with ν_{Q3}^{In}.

From the conclusive evidence that self-interstitials migrate freely already around 8 K,[7] we start our discussion by assigning the defects trapped at Pd during irradiation at 30 K to these self-interstitials.[8] Then two interpretations are conceivable for the defects trapped by the ^{111}In probes at 250 K: (i) a second type of interstitial and (ii) a vacancy-type defect.

Model (i) demands that the type-2 interstitials are formed by conversion of type-1 interstitials during migration at low temperatures. This model requires that such a conversion can occur in the vicinity of a vacancy or on trapping at an impurity.[9] The latter case is exactly what we can check with the Pd probe since the interstitials are trapped there. The experiment shows that detrapping occurs already at 100 K. This is the most likely process for the disappearance of the Pd signal and implies that the interstitials mobile at low temperatures cannot be converted into type-2 interstitials mobile at temperatures as high as 250 K.

Model (ii), on the contrary, does not lead to a difficulty in interpretation, Pd is an undersized atom in Nb,[10] while In is oversized. The strikingly discriminatory behavior of the two PAC probes may therefore be understood from the different strain fields generated in the Nb lattice. These generally make undersized atoms good trapping agents for interstitials,[11] whereas oversized atoms like In and Xe strongly attract vacancies, as observed in a variety of experiments. Though some cases are known where probes can trap both types of defects, in our case of *selective* trapping the general trend favors our interpretation of interstitial trapping at Pd and vacancy trapping at In.

In addition to the trapping behavior our results on the microscopic structure of the trapped defects strongly support the vacancy assignment. First, we point out, that the low-dose electron irradiation proves the long-range character of the defect migration and makes trapping of single defects the dominant process. We thus ascribe frequency ν_{Q1}^{In} to a probe having trapped a single defect. Frequency ν_{Q2}^{In} very likely represents a probe with a small defect cluster. The absence of ν_{Q3}^{In}, together with the large frequency spread of this component observed after heavy-ion irradiation, clearly shows that this defect has a more complex structure.

The measurement of the orientation of the EFG in the Nb single crystal provides detailed information on the "microscopic" structure of the trapped defect. Our result, ⟨111⟩ for the direction of ν_{Q1}^{In}, is exactly what one expects for a monovacancy as nearest neighbor to the In probe in the bcc lattice. In fact, this direction could recently be measured for a single vacancy as nearest neighbor to an ^{111}In probe in Mo.[12] In this case the assignment could be made since the vacancy migration temperature is unambiguously identified. The much-less-impurity-sensitive Mo metal allowed the application of PAC with ^{111}In probes using conventional doping techniques.

The results from all three parts of the experiment lead us to identify the interaction frequency ν_{Q1}^{In} with a single vacancy trapped at the ^{111}In probe. The available evidence on ν_{Q2}^{In}, including the measured asymmetry parameter $\eta_2^{\mathrm{In}} = 0.65$, strongly points to a trapped divacancy. Our PAC experiments on irradiated high-purity Nb with two different nuclear probes

TABLE I. PAC amplitudes s_n for ^{111}In in a Nb single crystal with the detectors pointing into ⟨111⟩. The calculated amplitudes for the z axis of the EFG pointing into the three main crystallographic axes are compared to experimental results for defect type ν_{Q1}^{In}.

	Theory			Experiment
	⟨100⟩	⟨110⟩	⟨111⟩	
s_1	0.367	0.326	0.461	0.490(30)
s_2	0.402	0.331	0.076	0.080(17)
s_3	0.231	0.093	0.134	0.124(18)

thus enable us to assign the frequencies appearing on annealing at 250 K to trapped vacancies. Comparison of heavy-ion and electron irradiation of several different Nb samples shows that this migration temperature is well defined and corresponds to long-range migration of single vacancies as low as 250 K.

ACKNOWLEDGMENTS

We are indebted to Professor H. Schultz (MPI Stuttgart) for providing the high-purity Nb samples and for helpful discussions. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 161).

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[10] A very recent experiment which directly produces ^{100}Pd in Nb without the intermediate ^{100}Ag confirms that Pd is indeed the trapping atom and not Ag.

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