Vacancy trapping and detrapping by ^{111}In implanted in Ni as observed by time-differential perturbed angular correlations

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With time-differential perturbed angular correlations on ^{111}In implanted in Ni, trapping and detrapping of vacancies has been observed in the temperature interval $20 \leq T \leq 400\,^{\circ}$C via isochronal annealing studies.

Nuclear techniques for measuring hyperfine interactions have proven to be useful for microscopic studies of radiation damage in solids. The most detailed information on defect configurations and their annealing behavior has so far been obtained from Mössbauer-effect measurements. For instance, the measurements of Mansel *et al.*[1] on ^{57}Co in Al subjected to fast-neutron irradiation have given clear indications of interstitial trapping and detrapping of Al atoms by Co impurities. Mössbauer measurements on implanted sources of ^{125}I, ^{131}I, and ^{133}Xe in Fe by de Waard *et al.*[2,3] have yielded information on vacancy trapping, which for these insoluble impurities is an irreversible process. Thus, annealing studies of *Fe* ^{133}Xe have shown that trapping increases with annealing temperature until all implanted Xe atoms are associated with vacancies.[3,4]

In this paper we report the first results of perturbed-angular-correlation measurements that give clear evidence of vacancy trapping by impurities, followed by detrapping at higher annealing temperatures. Our experiments employed implanted sources of ^{111}In in Ni, and involved observation of the time-differential-angular-correlation (TDPAC) spectrum of the well-known 175–247-keV γ-γ cascade of ^{111}Cd. Conclusions about trapping and detrapping were derived from the growth and subsequent disappearance of a low-frequency component in the spectrum.

Sources were made with the Groningen isotope separator by implanting 2.8-day ^{111}In into 25-μm-thick 99.998%-pure Ni foils at energies ranging from 5 to 130 keV, and total indium doses ranging from 10^{12} to 10^{14} atoms/cm^2. TDPAC spectra were obtained with three counters; for unmagnetized sources the quantity

$$R(t) = [C(\pi, t) - C(\tfrac{1}{2}\pi, t)]/[C(\pi, t) + 2C(\tfrac{1}{2}\pi, t) - 3B] \quad (1)$$

was derived; for sources magnetized perpendicular to the plane of the detectors

$$R'(t) = C(\tfrac{3}{4}\pi, t) - C(-\tfrac{3}{4}\pi, t)/[C(\tfrac{3}{4}\pi, t) + C(-\tfrac{3}{4}\pi, t) - 2B] \quad (2)$$

was obtained. Here $C(\theta, t)$ is the coincidence rate as a function of angle and delay and B is the accidental background.

For a single static magnetic hyperfine interaction of strength $\mu H_{\rm hf} = \hbar\omega_L I$, we expect, using conventional notation,[5] that

$$R(t) = (\tfrac{1}{10}A_{22})(2\cos 2\omega_L t + 2\cos\omega_L t + 1), \quad (3)$$

$$R'(t) = [3A_{22}/(4 + A_{22})]\sin 2\omega_L t, \quad (4)$$

where $A_{22} = 0.18$ and terms in A_{44} are suppressed.

A typical result for a magnetized source at room temperature is shown in Fig. 1. Both $R(t)$ and its Fourier transform indicate the presence of two sharply defined frequencies $2\omega_L$ and $2\omega_L^*$. These are found to recur to within statistical error in all sources investigated, and were shown to be associated with negative hyperfine fields $H_{\rm hf} = -66.9 \pm 0.03$ kG and $H_{\rm hf}^* = -27.3 \pm 0.7$ kG, respectively.[6] The former corresponds closely to results with diffused sources,[5] and is attributed to substitutional ^{111}In; the latter is assumed to arise from defect associated sites, the nature of which will be discussed below.

A total of five different sources were subjected to isochronal annealing sequences. In these, the sources were measured at room temperature directly after implantation, heated in vacuum to a temperature T_a, left there for 1 h, cooled, and remeasured at room temperature. Shown in Fig. 2 is part of a series of such measurements, in this case for an unmagnetized source. Multiparameter least-squares fits were made with the form

$$\begin{aligned} R(t) = A[&B\cos\omega_L(t - t_0)\, e^{-\lambda(t-t_0)} + (1 - B)\cos 2\omega_L(t - t_0) \\ &\times e^{-2\lambda(t-t_0)}] + A^*[B^*\cos\omega_L^*(t - t_0)\, e^{-\lambda^*(t-t_0)} \\ &+ (1 - B^*)\cos 2\omega_L^*(t - t_0)\, e^{-2\lambda^*(t-t_0)}] + \text{const}, \end{aligned} \quad (5)$$

with A, A^*, B, B^*, λ, λ^*, ω_L, ω_L^*, t_0, and const as free parameters. The amplitudes A and A^* describe the fractions of ^{111}Cd atoms associated with ω_L and ω_L^*, respectively, B, B^* describe the magnetic texture (for random magnetization we should

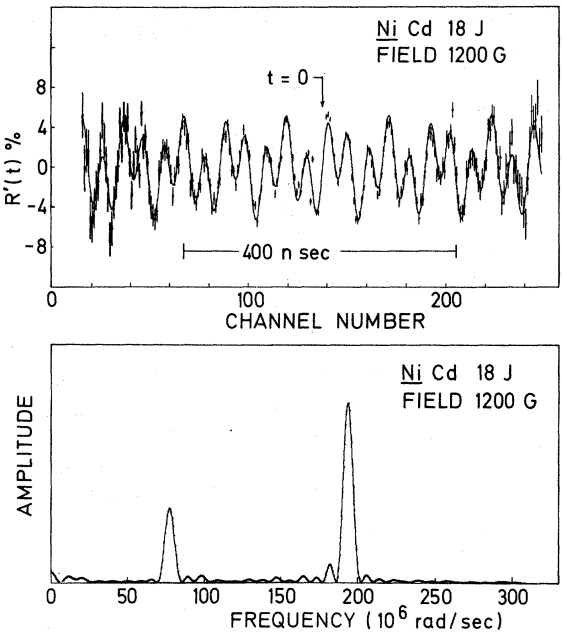

FIG. 1. Top: TDPAC spectrum of ^{111}IN implanted in Ni, after 30 min annealing at 230 °C. The source was magnetized perpendicular to the detector plane, and the data were fitted with the form $R'(t) = A' \sin 2\omega_L(t-t_0) + A'^* \sin 2\omega_L^*(t-t_0)$, with A', A'^*, ω_L, and ω_L^* as free parameters. Bottom: Fourier transform of the above time spectrum, showing the frequencies $2\omega_L$ and $2\omega_L^*$ found in the time spectrum.

have $B = B^* = 0.5$), and λ and λ^* allow for a loss of coherence. The presence of other frequencies was ruled out on the basis of Fourier analysis.

Qualitatively, the results for all sources were the same, and may be summarized as follows.

(i) For $T_a = 20$–100 °C, A^* increases and A decreases; for $T_a = 100$–300 °C, little change is observed; for $T_a > 300$ °C, A increases and A^* goes to zero. This behavior is shown graphically for two different sources in Fig. 3 and is interpreted as defect trapping for $T_a = 20$–100 °C, followed by subsequent detrapping above 300 °C. Evidently, there is no simple sum rule according to which $A + A^* = \text{const}$. We tentatively ascribe this to the fact that the degree of decoupling of the angular correlation, which depends on the texture parameters B and B^*, may be different for the defect-associated and substitutional sites.

(ii) A significant difference was found to exist between the texture coefficients B and B^*; on the average $B = 0.52 \pm 0.02$ and $B^* = 0.43 \pm 0.02$. This fact suggests that there is a difference in field distribution between the defect sites (with Larmor frequency ω_L^*) and the substitutional sites (Larmor frequency ω_L).

(iii) The damping constants λ and λ^* are small ($\lesssim 10^{-3}$/nsec). If they are indicative of inhomogeneous broadening, upper limits for the spread of frequencies around ω_L and ω_L^* may be derived from them: $\Delta\omega_L/\omega_L < 10^{-2}$ and $\Delta\omega_L^*/\omega_L^* < 5 \times 10^{-2}$.

(iv) The fraction $a^* = A^*/(A + A^*)$, measured immediately after implantation, depends on the implanted dose and the implantation energy: Dose-dependence results indicate a nonlinear variation of a^* with dose, suggesting that we are dealing with interacting damage sites.

(v) None of the spectra shows any influence of quadrupole interaction. This is best seen in Fig. 1, which illustrates that a theory based on magnetic interaction only gives an excellent fit to the data. In principle, a quadrupole interaction should

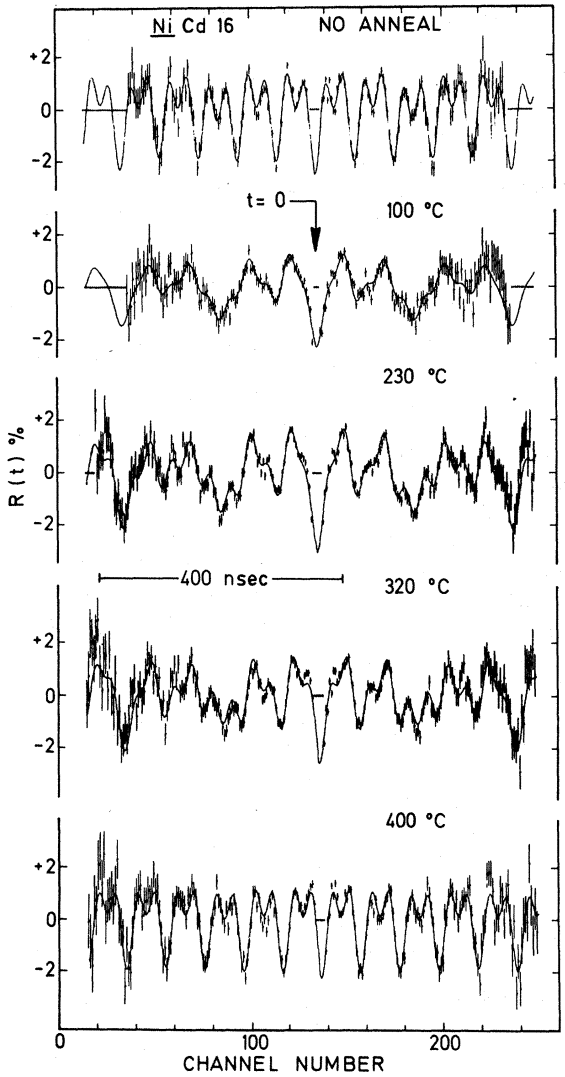

FIG. 2. Time-domain data for an unmagnetized source of ^{111}In implanted in Ni, illustrating the variation observed in an isochronal annealing sequence.

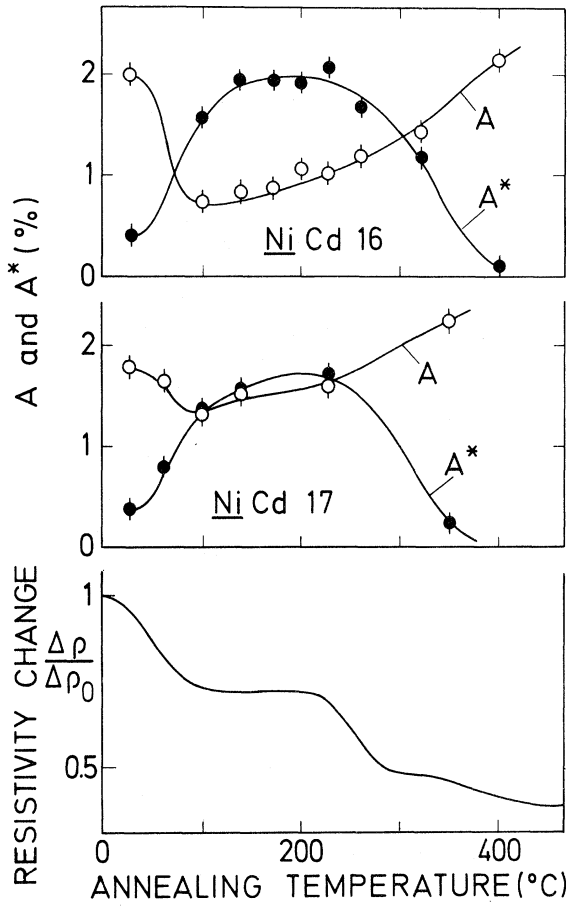

FIG. 3. Top and middle: Dependence of high- and low-frequency amplitudes on annealing temperature for two different sources. Bottom: Resistivity data for quenched Ni as given in Ref. 7.

be experienced by the defect-associated impurities, for which the cubic symmetry of the crystal is destroyed. Apparently the magnitude of this interaction is too small, compared with the magnetic interaction, to be observed.

The variation of A^* with T_a can be compared to the work of Scherrer and Deviot, [7] who measured the resistivity of quenched Ni in isochronal annealing sequences similar to our own. As seen in Fig. 3, the first of two discrete resistivity changes occurs at the place where we find rapid growth of A^*. Scherrer and Deviot assign this change to migration of divacancies which, because of a lower activation energy, become mobile at lower temperature than monovacancies. If Scherrer and Deviot are right, it is likely that our ω_L^* component is due to ^{111}In atoms associated with divacancies. Though present models for the hyperfine field[5] do not permit a quantitative interpretation of H_{hf}^*, the large reduction in field ($H_{hf}^*/H_{hf} = 0.4$) observed for our defect-associated site lends qualitative support to this conclusion. The second resistivity change seen in the quenching data increases with impurity content of the sample, and is thus interpreted by Scherrer and Deviot as vacancy detrapping from impurities. It is striking that their detrapping temperature coincides so well with ours, considering that their impurities were Cu and ours In.

Recently, another TDPAC measurement of defect association for ^{111}In in Ni has been reported by Andreeff *et al.* [8] In this case, recoil implantation at ~ 1 MeV was effected through the reaction ^{109}Ag $(\alpha, 2n)^{111}$In, using a Ni target on which a thin layer of Ag had been evaporated. After implantation, a spectrum much more complicated than ours was found. An annealing treatment shows no evidence for trapping and detrapping, but simply a cleanup of the spectrum, which at 600 °C resulted in observation of only the substitutional frequency.

We conclude that the study of magnetic hyperfine interaction strengths and amplitudes by TDPAC provides in the case of *Ni* ^{111}In a sensitive indicator of defect migration. In order to make a unique assignment of defect sites, however, further investigations are required.

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