Perturbed angular correlation study of impurity interactions in a cubic host metal: Hf in Nb

W. H. Warnes* and J. A. Gardner
Department of Physics and Advanced Materials Research Center, Oregon State University, Corvallis, Oregon 97331
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^{181}Ta perturbed angular correlation experiments have been performed on Nb-Hf alloys containing 0.5–5.5 at. % Hf. A Maxwellian frequency distribution model is proposed to account for the electric-field-gradient distribution due to impurities in a cubic matrix. The model was used to analyze the Nb-Hf data. If an unperturbed fraction is included with the Maxwellian distribution, then agreement with experiment is excellent. The unperturbed site is apparently required to correct for underestimation of the actual distribution by the Maxwellian at low frequencies. The unperturbed fraction is large only for small impurity concentrations and corresponds approximately to sites more distant than five lattice spacings from the nearest impurity. The peak of the Maxwellian quadrupole frequency distribution is linear in Hf concentration.

INTRODUCTION

The γ-γ perturbed angular correlation (PAC) technique is useful for studying electric fields in condensed matter through the interaction between the probe nuclei and the electric field gradient (EFG) at the nuclear site.[1,2] It has been applied to a variety of studies of noncubic metals and alloys,[3] semiconductors,[4] and ceramics.[5] Most experimental work has been concerned primarily with situations in which the PAC tracer nucleus is subjected to a nonzero magnetic or electric interaction. This includes a considerable body of work on cubic metals[6,7] for which the interaction is due to an EFG caused by defects localized near the tracer atom. Some important PAC measurements have also revealed asymmetric lattice distortions around Cd in Si and Ge,[8,9] where without such a distortion the EFG should be zero even though the symmetry is less than cubic. There is some interest in studying site occupancies, dynamic interactions, and distant interactions with random imperfections in defective cubic materials where the EFG at the PAC probe nucleus is zero on average.[10–14] This work is intended in part to establish an appropriate phenomenological framework for modeling such situations. It is also intended as the first in a series of experiments in our laboratory on niobium alloys and intermetallic compounds.

In PAC experiments, trace levels of radioactive impurities such as ^{181}Hf or ^{111}In are introduced into the sample of interest. Two gamma rays emitted during the decay process are detected, and their angular anisotropy is measured as a function of the time between the emission of the two gamma rays. This anisotropy is experimentally described by a function $A_2G_2(t)$, where A_2 is an effective anisotropy, and $G_2(t)$ is a function representing the modulation of the anisotropy by the nuclear electric quadrupole interaction. It is similar in physical content to the free induction decay of a nuclear quadrupole resonance measurement. The PAC methodology[1,5] and experimental apparatus[15] have been described elsewhere.

In the work described here, the PAC spectrum is determined for ^{181}Ta impurities in Nb metal containing up to 5.5 at. % Hf in solid solution. The ^{181}Ta results from β^- decay of ^{181}Hf that is produced from naturally occurring ^{180}Hf by neutron irradiation of the samples. Spectra are recorded for samples as received with a significant degree of cold work and again after a vacuum annealing heat treatment. The PAC spectrum is characterized by a broad quadrupole frequency distribution whose average and range are larger for cold worked than for annealed samples and which increase with Hf content.

Common models incorporating Gaussian or Lorentzian broadening for PAC analysis of imperfect noncubic materials are physically reasonable only when the broadening is small with respect to the average.[1] Since niobium has cubic symmetry, the only EFG at a ^{181}Ta impurity is due to defect interaction effects, and these models are not applicable. We propose a generalization of the Gaussian-broadening model which takes into account the three-dimensional distribution of EFG's and that can be evaluated easily when the unperturbed EFG is zero. In this limit, the frequency distribution is Maxwellian. In the following sections we discuss the PAC experimental data, the motivation and description of the Maxwellian model, and its application to the experimental data. The experimental frequency distribution of samples with large impurity concentration is well described by the model, but in more dilute samples a significant fraction is found to be less strongly perturbed. Excellent computer fits are obtained if some fraction of the Ta nuclei are assumed to be unperturbed. The unperturbed fraction is found to correspond to nuclei having no impurities within approximately five lattice spacings. The peak frequency ω_0 of the Maxwellian distribution function is proportional to the Hf concentration.

THE MAXWELLIAN MODEL

In most hyperfine experiments, the nuclear levels are split by a large magnetic or quadrupolar interaction that has only minor spatial variations. The experimentally determined frequency distribution is usually well approximated by a Gaussian whose width is a measure of the

strength of the local variations. For PAC spectra in noncubic materials, a common approximation is to neglect variations in the asymmetry parameter, η, and assume a Gaussian distribution of the EFG magnitude V_{zz} about the average, V_{zz}^0. This approximation is physically reasonable as long as the Gaussian width is small with respect to V_{zz}^0. For the case of PAC in imperfect cubic lattices, this provision is violated. The average EFG is zero, but the interaction frequency (which is conventionally taken as positive) does not average to zero. A physically reasonable approximation for these experiments must take proper account of the three-dimensional distribution of the EFG principal axes.

The simplest assumption is that the principal EFG axes are randomly oriented, that η is fixed, and that the projection of V_{zz} on all three Cartesian axes has a Gaussian distribution centered on zero with width V_{zz}^0. It follows immediately that the distribution of the magnitude of V_{zz} is Maxwellian:

$$P(|V_{zz}|)d|V_{zz}|=\frac{4}{\sqrt{\pi}(V_{zz}^0)^3}V_{zz}^2 \times\exp[-(|V_{zz}|/V_{zz}^0)^2]d|V_{zz}| \ . \quad (1)$$

The PAC time-development function, $G_2(t)$, for ^{111}Cd nuclei subject to randomly oriented EFG's of magnitude $|V_{zz}|$ and asymmetry η is given by[1]

$$G_2(t)=S_0+\sum_{k=1}^{3} S_k\cos(\omega_k t) \ , \quad (2)$$

where $\omega_k=\alpha_k|V_{zz}|$, α_k and S_k are functions of η, $\omega_1\le\omega_2\le 2\omega_1$, and $\omega_3=\omega_1+\omega_2$. It follows that the shape of the ω_k distribution is the same as that of $|V_{zz}|$. For the Maxwellian distribution, then,

$$\begin{aligned} G_2(t)&=S_0+\frac{4}{\sqrt{\pi}}\sum_{k=1}^{3}\frac{S_k}{\omega_{k0}^3}\int_0^\infty \omega^2\exp[-(\omega/\omega_{k0})^2]\cos(\omega_{k0}t)d\omega \\ &=S_0+\sum_{k=1}^{3} S_k(1-\omega_{k0}^2t^2/2)\exp(-\omega_{k0}^2t^2/4) \ , \end{aligned} \quad (3)$$

where $\omega_{k0}=\alpha_k|V_{zz}^0|$.

EXPERIMENTAL PROCEDURE AND RESULTS

Experimental procedure

Five samples with Hf content between 0.2 and 5.5 at. % Hf were measured (see Table I). Hf has a very large solid solubility in Nb (> 40 at. %), so that all the samples were single-phase substitutional solid solutions.

The samples were prepared by arc melting from a commercial niobium alloy (TWCA-C103, containing 5.5 at. % Hf, 0.5 at. % Zr, 0.2 at. % Ta, and 1.9 at. % Ti) to which high-purity Nb was added to dilute the Hf content to the desired level. A Nb-Hf/bronze composite wire made from the TWCA-C103 material was also studied. The impurity content for each sample was determined by chemical analysis, and is given in Table I. All of the samples studied had negligible oxygen contamination.

The alloys were cold rolled to form foils approximately 0.004 in. thick from which small samples of about 0.5 g were cut. The wire sample was more strongly cold worked than the foils due to the wire drawing process. The wire was cut to a length which provided an amount of Hf comparable to the 5.5 at. % foil sample.

All samples were sealed in separate evacuated fused-silica capsules, and neutron-irradiated at the Oregon State University TRIGA reactor to produce 1–10 μCi of ^{181}Hf activity. The PAC spectrum was then measured in the cold-worked condition at room temperature (designated by CW in the analysis). Most samples were then annealed for 1 h at 1050 °C to remove the cold work and any radiation damage, and the PAC spectrum was again measured (designated as AN in the analysis). One of the

TABLE I. The Nb-Hf binary samples. Numbers in parentheses indicate the absolute uncertainties in the fit parameters.

Sample	at. % impurity	Fitting parameters ω_0 (mrad/s)	f (%)	History
Nb–0.2 at. % Hf CW	0.27	34.9(1.8)	74.6(2.8)	Cold worked
Nb–0.5 at. % Hf 1 CW	0.84	39.2(1.0)	86.1(1.6)	Cold worked
Nb–0.5 at. % Hf 1 AN	0.84	22.3(1.2)	53.0(3.1)	1×1/1050
Nb–0.5 at. % Hf 2 CW	0.84	39.8(1.5)	86.1(2.1)	Cold worked
Nb–0.5 at. % Hf 2 AN	0.84	22.7(1.5)	48.5(3.4)	1×1/1050
Nb–1.5 at. % Hf CW	1.78	62.2(0.7)	87.9(0.5)	Cold worked
Nb–1.5 at. % Hf AN	1.78	40.8(0.6)	78.0(0.7)	1×1/1050
Nb–1.5 at. % Hf AN2	1.78	40.6(0.8)	76.5(0.9)	2×1/1050
Nb–5.5 at. % Hf CW	8.40	122.2(1.5)	94.2(0.5)	Cold worked
Nb–5.5 at. % Hf AN	8.40	106.3(1.0)	93.3(0.4)	1×1/1050
Nb–5.5 at. % Hf wire CW	7.40	146.8(2.3)	91.0(0.5)	Cold worked

samples was given a second anneal (AN2) to determine the effect of continued annealing on the spectrum. No noticeable difference was found between the one- and two-hour annealed samples.

Experimental results

The time spectra and the corresponding Fourier spectra for the highest and lowest concentration annealed samples are shown in Figs. 1 and 2. The experimental frequency spectrum of Fig. 2(a) is a broad asymmetric peak with an approximately Maxwellian shape. The Fourier spectra of the other AN samples are similar, but the broadening and peak frequency are smaller [Fig. 2(b)]. The low-impurity samples show qualitatively similar time spectra to the spectrum of Fig. 1(a), though the statistical error increases as the Hf content decreases [Fig. 1(b)].

Since none of our samples contained significant oxygen contamination, we did not find the Ta-O complexes studied by Wrede *et al.*[7] Klyucharev *et al.* have also made PAC measurements in the Nb-Hf system,[10,11] and our experimental spectra are in reasonable agreement with theirs.

Computer fits to the Maxwellian model generally converged with η values between 0 and 0.3. The fit was not greatly sensitive to η, and we chose to fix η to zero in order to minimize the number of fitting parameters. The geometrical parameters (S_1,S_2,S_3) are functions of η only, and are fixed for a constant value of η. By setting $\eta=0$ we define $\omega_{10}=\omega_0$, $\omega_{20}=2\omega_0$, and $\omega_{30}=3\omega_0$, and we are left with only two fitting parameters for the single-site Maxwellian fits [Eq. (3)]: A_2 and ω_0. The single-site fits were good for the high-impurity content samples (see Fig. 1).

For lower-impurity content samples, however, no single-site Maxwellian fit was adequate. This model apparently underestimates the density of sites with negligible impurity broadening, so an unperturbed fraction was

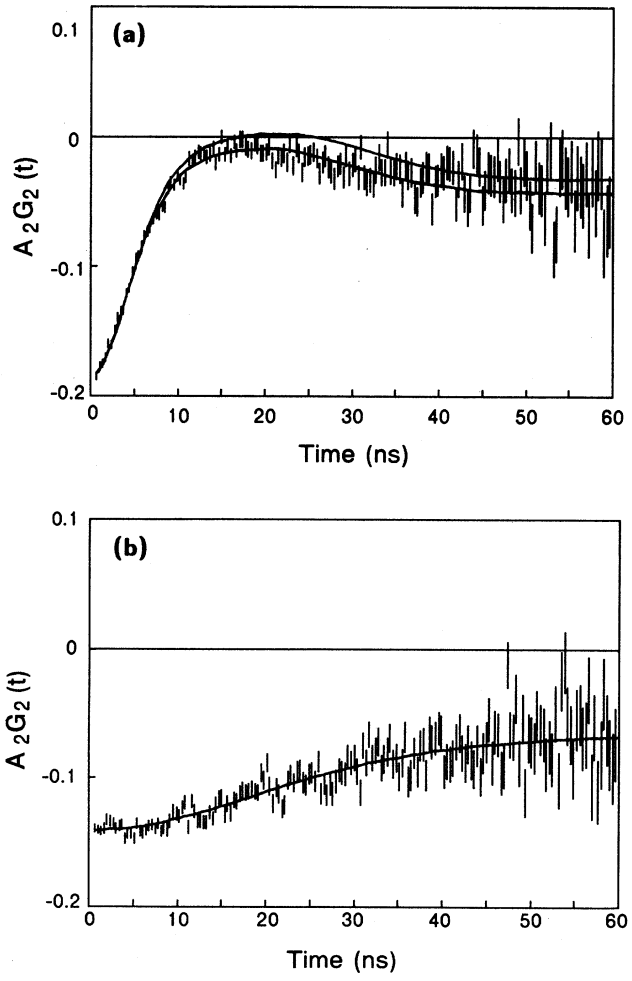

FIG. 1. The PAC time spectrum for the annealed samples (a) Nb–5.5 at. % Hf AN, fit by Eq. (3) (upper solid line) and Eq. (4) (lower solid line) as discussed in the text, and (b) Nb–0.5 at. % Hf AN, fit by Eq. (4).

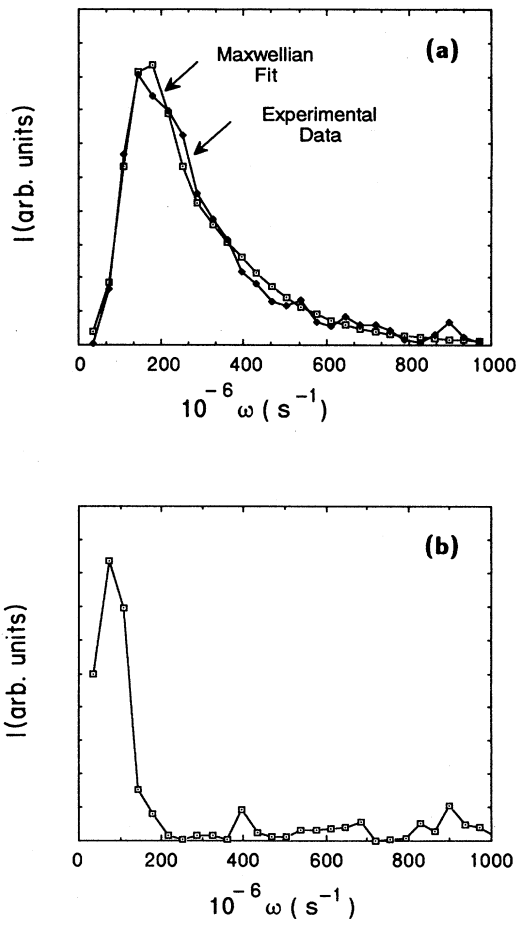

FIG. 2. Fourier transforms of the (a) Nb–5.5 at. % Hf AN spectrum and the (b) Nb– 0.5 at. % Hf 1 AN spectrum showing the broadened Maxwellian distribution of EFG. Also shown in (a) is the Fourier transform of the computer fit [Eq. (4)] shown in Fig. 1(a). Both plots in (a) use the same vertical scaling factor.

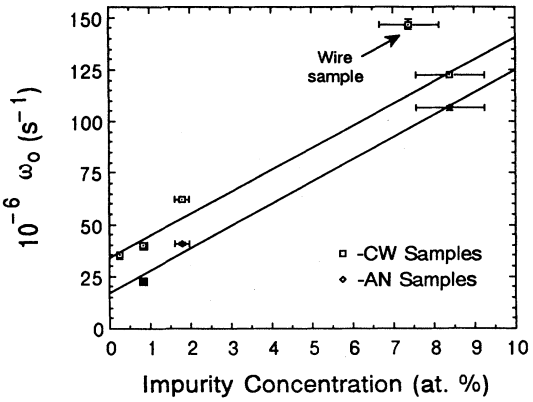

FIG. 3. The peak frequency, ω_0, vs Hf content as determined by fits of the experimental data using the Eq. (4). The two data sets are for the CW and AN samples.

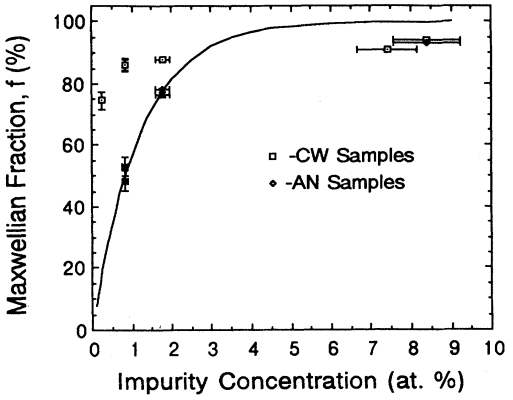

FIG. 4. The Maxwellian fraction, f, as a function of Hf content as determined by fits of the experimental data using Eq. (4). The two data sets are for the CW and AN samples. The solid line is the probability of finding an impurity atom within a sphere of reduced radius r/a of the PAC probe atom, where a is the bcc lattice parameter. A one-parameter fit was performed using the low-impurity data, and yielded a reduced radius of $r/a=4.4$ for the annealed samples.

added, where for $\eta=0$,

$$G_2(t)=(1-f)+fS_0+f\sum_{k=1}^{3}S_k(1-k^2\omega_0^2t^2/2)\times\exp(-k^2\omega_0^2t^2/4)\ . \quad (4)$$

This addition adds a third parameter, f, the fraction of sites in the Maxwellian distribution. It is evident from Figs. 1(b) and 2(a) that this model provides an excellent fit to the data. For all samples tested, the experimentally fitted values for A_2 were consistent with values expected for this isotope and the spectrometer geometry.

The results of fitting the data with Eq. (4) are given in Table I. Figure 3 shows the peak frequency, as a function of impurity content. The Nb–1.5 at. % Hf AN and Nb–1.5 at. % Hf AN2 samples have the same spectra and fitting parameters, indicating that a 1 h anneal at 1050 °C is sufficient to remove the cold-work disorder.

Figure 4 shows the Maxwellian fraction as a function of impurity content. The fraction f is large and approximately constant above 1 at. % in the cold-worked samples, and 3 at. % in the annealed samples.

DISCUSSION AND CONCLUSIONS

It can be seen from these data that the two-site Maxwellian model [Eq. (4), with three variable parameters] fits the data very well. The small value of $1-f$ implies that the Maxwellian shape is an almost but not completely accurate model at high-impurity concentrations. At lower-impurity concentrations, the Maxwellian distribution apparently overestimates the effects of distant impurities. The functional form of f at low concentrations suggests that for the annealed samples, impurity effects beyond about 4.5 lattice spacings are negligible.

It is seen from Fig. 3 that the peak frequency (ω_0) varies approximately linearly with impurity concentration C. In the cold-worked foil samples, ω_0 is uniformly about 20 Mrad/s larger than for the annealed foils. The larger values of ω_0 and f for the CW foils are probably due to the presence of additional cold work. The Nb–5.5 at. % Hf wire sample, which contains the most cold work, also exhibits the largest value of ω_0.

The significance of the linearity of ω_0 with C is not clear. However, we expect the second moment, $\langle\omega^2\rangle$, to scale with C. This dependence has been shown to be rigorously correct for random dipolar interactions,[16] and should hold for most random isotropic perturbations. The second moment for our model, $f\omega_0^2$, is roughly linear in C, as expected.

The quadrupolar interactions with impurities that are observed in this experiment are comparable in magnitude to those measured in cubic insulators and modeled successfully by electrostatically interacting point ions.[5,12] Point-ion calculations for metals including screening yield interactions that are at least an order of magnitude too small.[17] Therefore, it is probable that the interactions in Nb-Hf are due to the strain field around the impurities rather than electrostatic interactions.

These observations can be summarized as follows:

(1) The broadened PAC spectrum in imperfect cubic materials is well fitted by a distribution of EFG's with a Maxwellian shape plus a fraction of unperturbed sites.

(2) There is a linear dependence of the peak frequency upon the impurity content.

(3) The majority of the broadening measured in Nb-Hf binary alloys is attributed to the effects of lattice strain caused by the presence of the impurity atoms.

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*Present address: Department of Mechanical Engineering, Oregon State University, Corvallis, OR 97331.

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