PAC PERTURBATION FACTOR FOR SPIN 5/2 NUCLEI SUBJECT TO A RAPIDLY
FLUCTUATING EFG¹ DOE/ER/45191--14

DE91 005569

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We report numerical computations of the PAC perturbation factor $G_2(t)$ for spin 5/2 nuclei subject to a static EFG symmetric about the z-axis and an additional axially-symmetric EFG whose symmetry axis fluctuates randomly among the x, y, z directions. For sufficiently large fluctuation rates, the numerical results are described by the expression for the static interaction alone with the addition of relaxation terms. Results of applying this model to ^{111}Cd TDPAC measurements on tetragonal ZrO_2 are described briefly. The model allows one to evaluate the probability that oxygen vacancies are trapped, the energy of association of vacancy-metal pairs, and the vacancy activation energy of motion.

I. INTRODUCTION

In the case of rapidly changing environments, the interpretation of perturbed angular correlation (PAC) spectra from solids is rather complicated. This situation can occur when rapidly moving defects such as vacancies contribute significantly to the hyperfine fields experienced by the probe nucleus. Then the stochastic theory of the PAC spectrum due to Blume /1/ and Winkler and Gerdau /2/ allows one to obtain physical information about the solid and the properties of the defects from PAC experiments. PAC spectra affected by rapidly moving defects have commonly been fit heuristically to static PAC spectra augmented by nuclear relaxation and line broadening terms. Unfortunately, the connection between the heuristic relaxation and line broadening parameters and the physical properties of the defects is obscure, at best.

The present work reports a model calculation that is appropriate for a wide range of experimental situations where a rapidly-moving impurity or vacancy causes the EFG to fluctuate. This model calculation elucidates the physical origin of the heuristic relaxation and line broadening parameters, providing a theoretical basis for such heuristic fits and for the interpretation of these parameters in terms of the properties of the rapidly moving defects. One can then obtain information from PAC spectra about the hyperfine fields in the solid, the relative populations of various configurations of hyperfine fields, and hence of distributions of defects or local environments, and the defect jump rate in the solid.

In section II we describe the model and the physical picture which motivates it. In section III we describe the calculation of the PAC spectrum for the model and give the results of the calculation. In section IV we give a brief report of the application of this work to experimental PAC results for zirconia.

II. THE MODEL

We have made numerical calculations of the PAC perturbation factor $G_2(t)$ for spin 5/2 nuclei subject to a fluctuating electric field gradient (EFG). The model assumes a static EFG that is symmetric about the z-axis and an additional axially-symmetric EFG whose symmetry axis fluctuates randomly among the x, y, and z directions. Perturbation factors were computed as functions of fluctuation frequencies for several values of $k \equiv V_{zz}(\text{fluctuating})/V_{zz}(\text{static})$, including $k = 1, 10$, and 100 , using the method described by Winkler and Gerdau /2/.

III. CALCULATION AND RESULTS

By the method of Winkler and Gerdau /2/, we calculate the PAC perturbation factor $G_2(t)$, assuming the three states (i.e. the three directions of the fluctuating EFG) to be equally probable, so

¹Supported in part by USDOE contract DE-FG06-85ER45191

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$p_a = 1/3$ for $a = 1, 2, 3$, and the perturbation factor for a polycrystalline source is given by the following expression:

$$G_2(t) = \sum_{m_1, m_2, N} (-1)^{2I+m_1+m_2} \begin{pmatrix} I & I & 2 \\ m_1' & -m_1 & N \end{pmatrix} \begin{pmatrix} I & I & 2 \\ m_2' & -m_2 & N \end{pmatrix} \times \sum_{a,b} p_a (b m_2 m_2' | e^{(-\frac{i}{\hbar} \mathcal{H}_{st}^X + \hat{R})t} | a m_1 m_1') \quad (1)$$

where $(-\frac{i}{\hbar} \mathcal{H}_{st}^X + \hat{R})$ is the Blume matrix, defined as in Ref. 2: $\mathcal{H}_{st}^X$ is the Liouville operator composed of the three static hyperfine interaction Hamiltonians representing the three EFG states through which the system fluctuates, and $\hat{R}$ is the Liouville relaxation operator for three states with equal transition probabilities.

We calculate eigenvalues and both left and right eigenvectors for the Blume matrix to obtain the following expression for the perturbation factor:

$$G_2(t) = \sum_q G_2(q) e^{(-\lambda_q + i\omega_q)t} \quad (2)$$

i.e. a sum of terms corresponding to the complex eigenvalues of the Blume matrix. Each of the complex eigenvalues has its own frequency, ω_q , and relaxation rate, λ_q . For the above model, taking

Fig. 1. (a) Primary PAC frequencies and (b) primary PAC relaxation rates as functions of the EFG fluctuation rate for $k = 100$.

Fig. 2. PAC spectra for ^{111}Cd in 0.3 at.% Y-doped tetragonal ZrO_2 . Both frequencies and damping change with temperature due to the temperature-dependence of oxygen vacancy (V_O) jump rate and Cd- V_O trapping probability.

Fig. 3. ^{111}Cd relaxation rate due to a trapped oxygen vacancy. The solid lines are computer fits to the data.

account of the symmetry of the system, there are in general 25 distinct complex eigenvalues. However, for sufficiently slow or sufficiently fast fluctuation rates, the only frequencies which contribute to the perturbation factor with significant weight are those which correspond to the appropriate static interaction alone. That is, for slow fluctuation rates, the "fluctuating" EFG is static, and the perturbation factor is due to the superposition of the resulting three static EFGs in the model. For rapid fluctuation rates, on the other hand, the fluctuating EFG changes orientation too fast to be seen by the probe, and the frequencies are those of the model's static EFG alone. Nevertheless, there are significant relaxation terms in the perturbation factor for rapid fluctuation rates, due to the Abragam-Pound-like $/3/$ limit of the fluctuating EFG.

Because of space limitations we report numerical results here only for the case $k = 100$. We are submitting details of our calculations for other values of k for publication elsewhere.

For $k = 100$ the PAC frequencies which enter $G_2(t)$ with a weight of at least 6% are shown in Fig. 1(a). Note that, as explained above, for sufficiently slow or sufficiently rapid fluctuation rates, the frequencies which appear are close to those which arise from the appropriate static interaction. In the intermediate fluctuation rate regime, the perturbation factor is composed principally of relaxation terms.

The PAC relaxation rates for $k = 100$ which enter $G_2(t)$ with a weight of at least 6% are shown in Fig. 1(b). The relaxation rates for rapid fluctuations vary strongly with the fluctuation rate, so that observation of the PAC relaxation rate gives a good measure of the physical jump rate which is responsible for the EFG fluctuations.

In the rapid fluctuation regime, the numerical results for all k are described by

$$G_2(t) = s_{20} e^{-\lambda_0 t} + s_{20}' e^{-\lambda_0' t} + \sum_{i=1}^3 s_{2i} \cos(\omega_i t) e^{-\lambda_i t} \quad (3)$$

where $s_{20} = 0.131$, $s_{20}' = 0.069$, the other geometrical factors s_{2i} and frequencies ω_i are the same as for the static interaction alone. The ratios $\lambda_0 : \lambda_0' : \lambda_1 : \lambda_2 : \lambda_3 = 1 : 3.52 : 2.34 : 3.07 : 5.90$, and $\lambda_0 = 100.8 \langle \omega_Q^2 \rangle \tau_c$, which is the Abragam-Pound relaxation rate $/3/$ for the fluctuating EFG alone. ω_Q is the quadrupole frequency corresponding to the fluctuating EFG, and $w = 2\pi/\tau_c$ is the EFG fluctuation frequency.

IV. APPLICATION TO ZIRCONIA

When ZrO_2 is lightly doped with Y or In (1000–1400 C), each impurity atom introduces half an oxygen vacancy to achieve charge balance. We have used this model to fit ^{111}Cd PAC spectra $/4/$, illustrated in Fig. 2. We show that the ^{111}Cd PAC probes trap oxygen vacancies with an association energy of 0.8(1) eV. When a vacancy is bound to a ^{111}Cd impurity, the vacancy hops among 8 nearest-neighbor anionic sites causing the relaxation shown in Fig. 3. The slope of λ gives the hopping energy barrier of 0.8(1) eV.

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