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DOE/ER/45191-16

PAC ANALYSIS OF DEFECT MOTION BY BLUME'S

STOCHASTIC MODEL FOR $I = \frac{5}{2}$ ELECTRIC

QUADRUPOLE INTERACTIONS

DOE/ER/45191--16

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ABSTRACT

Using Blume's stochastic model and the approach of Winkler and Gerdau, we have computed time-dependent effects on perturbed angular correlation (PAC) spectra due to defect motion in solids in the case of $I = \frac{5}{2}$ electric quadrupole interactions. We report detailed analysis for a family of simple models: "XYZ+Z" models, in which the symmetry axis of an axial efg is allowed to fluctuate among orientations along x , y , and z axes, and a static axial efg oriented along the z axis is added to the fluctuating efgs. When the static efg is zero, this model is termed the "XYZ" model. Approximate forms are given for $G_2(t)$ in the slow and rapid fluctuation regimes, i.e. suitable for the low and high temperature regions, respectively. Where they adequately reflect the underlying physical processes, these expressions allow one to fit PAC data for a wide range of temperatures and dopant concentrations to a single model, thus increasing the uniqueness of the interpretation of the defect properties. Applications of the models are given for zirconia and ceria ceramics.

I. INTRODUCTION

Perturbed angular correlation (PAC) spectra in solids are sensitive, local measures of the atomic environment of probe nuclei via hyperfine interactions. For the study of defects in solids, PAC provides an important and useful technique by which one can infer species, positions, numbers, motions, and interactions with other species or with the host material. Unfortunately, any one of these spectra can usually be fitted by several simple models which reflect the hyperfine parameters of the spectrum but which do not have an obvious relationship with the underlying physical processes. The object of these experiments is, of course, physical understanding, not just fitting spectra. More sophisticated models, which include the effects of fluctuating electric field gradients (efgs) due to moving defects, allow the fitting of many spectra at once, covering a wide range of temperatures and dopant concentrations, with a single model. In this case, the fits may be sufficiently constrained that they become nearly unique, allowing much greater confidence in the physical interpretation of the data. The stochastic theory of the PAC spectrum due to Blume [1] and Winkler and Gerdau [2] provides the means of developing such models which are appropriate to the study of defects in solids.

In section II we describe the family of models we have studied and the calculation of the PAC spectrum for these models in the case of $I = \frac{5}{2}$ electric quadrupole interactions. $I = \frac{5}{2}$ is an important special case since most PAC studies are done using ^{111}Cd or ^{181}Ta probes, both of which have an intermediate state spin $\frac{5}{2}$. In section III we give the results of the model calculations. Section IV contains a brief report of the application of this work to experimental PAC results for zirconia and ceria. Section V provides a summary and

conclusions.

II. XYZ AND XYZ+Z MODELS

Winkler and Gerdau [2] developed an approach for calculating PAC spectra using Blume's stochastic theory of PAC. Their formulation has been applied to some simple models which reflect the physics of defect motions in solids. In the case of $I = \frac{5}{2}$ electric quadrupole interactions, Winkler and Gerdau did some illustrative calculations for a model consisting of fluctuations among three axial efgs oriented along the x , y , and z directions, respectively. We refer to this model, parameterized by w , the probability per unit time for transitions from one efg to another, as the XYZ model. The probability of jumping between each pair of efg states is taken as equal, so there is a single parameter w . We also add a static axial efg with axis along the z direction to the XYZ model, giving a family of XYZ+Z models parameterized by the jump frequency of the fluctuating efgs, w , and the ratio of static V_{zz} to fluctuating V_{zz} , γ . The XYZ model is then just the XYZ+Z model for $\gamma = 0$.

These models should apply to PAC studies of moving defects in materials when the defect is trapped in an atomic shell near the probe, so the efg due to the defects is approximately axially symmetric and fluctuates primarily by changing the direction of the symmetry axis, but does not change significantly in size. The background efg due to the lattice or static defects will contribute a static term, taken as axially symmetric as a first approximation in the models. Other situations in which the fluctuating efgs due to defect motion are axially symmetric to a first approximation can also be studied by these models. In addition, the simplified forms given below provide guidance for heuristic models that might be employed

when the efgs in question are not axially symmetric. *E.g.* where static coefficients and frequencies appear, they can be replaced by their appropriate values for nonzero η as a zeroth order approximation. The number of efg states, N , among which the system fluctuates will have a quantitative effect on the spectra, but it should not make a qualitative difference. Different values of N are taken approximately into account in the relaxation rates by scaling as $(N-1)w$ for small w (below the relaxation peak) and as $1/Nw$ for large w (above the peak) [3].

Relaxations of PAC spectra have been studied in similar models by Baudry and Boyer [3] who proposed the use of heuristic isotropic models like those of Abragam and Pound [4] and Marshall and Meares [5] to approximate PAC spectra in the XYZ model and in a four-state model similar to the XYZ+Z model. The four-state model studied by Baudry and Boyer differs from the XYZ+Z model by having four fluctuating efgs rather than three. In addition, in their model the static efg apparently has its axis of symmetry oriented symmetrically with respect to all four fluctuating efgs, giving four equivalent efg states and hence higher symmetry than is true of the XYZ+Z models.

Andrade *et al.* [6] studied models which are similar to the $\gamma = 0$ and large γ XYZ+Z models in the rapid fluctuation limit.

We describe below our calculation of $G_2(t)$ for these models and give analytic expressions, where a wider range of parameters has been considered than for the Baudry and Boyer approximation or the Andrade *et al.* case. The expressions given here lead to accurate determination of the physical parameters if sufficient data are available. Evenson *et al.*

[7]¹ have previously given a rapid fluctuation (high temperature) expression for the case $\gamma = 0.01$ and applied it to zirconia ceramics. In this paper we also clarify the γ -dependence of the models.

Much of the difficulty of applying the method of Winkler and Gerdaun has been due to the necessity of finding complex eigenvalues and both left and right eigenvectors of a large non-Hermitian matrix. For the XYZ+Z family of models, one obtains a 108×108 matrix. However, in this case, the matrix is complex symmetric, giving a simple relation between the left and right eigenvectors:

$$(N_q^k | = (M_q^k |^*, \quad (1)$$

where $|M_q^k\rangle$ are the right eigenvectors for the q^{th} eigenvalue, and k is a degeneracy index. [$(M_q^k |$ is, of course, the Hermitian conjugate of $|M_q^k\rangle$.] This notation is that of [2] with the addition of the degeneracy index. When one includes degeneracy, the perturbation factor for a polycrystalline sample with random crystallite orientations becomes:

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

$$G_q \equiv \sum_{m_1 m_2 p} (-1)^{2I+m_1+m_2} \begin{pmatrix} I & I & 2 \\ m'_1 & -m_1 & p \end{pmatrix} \begin{pmatrix} I & I & 2 \\ m'_2 & -m_2 & p \end{pmatrix} \\ \times \sum_{abk} p_a (bm_2 m'_2 | M_q^k) (N_q^k | am_1 m'_1). \quad (3)$$

¹Note that the value of λ_0 quoted in that paper is missing a factor of 2.72. It should be given as $2.72\lambda_0 = 100.8\langle\omega_Q^2\rangle\tau_c$.

In addition, the symmetry of this case, which makes the static energies of each of the component efgs degenerate for $\pm m$ [8], introduces a fourfold degeneracy in all the eigenvalues of the models. Therefore, one can calculate the eigenvalues and right eigenvectors for a reduced 27×27 matrix, speeding the calculation considerably. (Eigen calculations increase time demands as about N^3 , so this provides a factor of about 64 in computational speed.) The final computation of G_q is made slightly more complicated by this reduction to a 27×27 matrix and must now be carried out as follows:

$$G_q = 2 \sum_{m_1 m_2} \sum_{p=-2}^2 \begin{pmatrix} \frac{5}{2} & \frac{5}{2} & 2 \\ m'_1 & -m_1 & p \end{pmatrix} \begin{pmatrix} \frac{5}{2} & \frac{5}{2} & 2 \\ m'_2 & -m_2 & p \end{pmatrix} \times \sum_{abk} p_a (bm_2 (-1)^p m'_2 | M_q^k) (N_q^k | am_1 (-1)^p m'_1), \quad (4)$$

where the m_1 and m_2 sums go only over the values $-\frac{5}{2}, -\frac{1}{2}, \frac{3}{2}$.

We have computed $G_2(t)$ for $0 \leq \gamma \leq 100$ and $0 \leq w \leq 10^7$, calculating the eigenproblem by the Q-R triangularization method with the COMQR2 subroutine of EISPACK [9]. We have used both the FORTRAN program from EISPACK and a C translation of it and have calculated $G_2(t)$ on several computers, including VAX 11/780, Ridge workstation, HP-9000/835 workstation, and 386-20 microcomputer with math coprocessor. On the 386-20 microcomputer, the calculation of $G_2(t)$ typically requires about 25 seconds for a single value of w and γ .

III. RESULTS

In general the complex eigenvalues of the Blume matrix have both real parts (λ_q , relaxation rates) and imaginary parts (ω_q , electric quadrupole splitting frequencies). Each eigenvalue

enters $G_2(t)$ with complex coefficient G_q , so if $\omega_q = 0$, there is a relaxation term of the form $e^{-\lambda_q t}$ which makes a contribution to $G_2(t)$ of relative magnitude $|G_q|$. If $\omega_q \neq 0$, the two terms $G_q e^{(-\lambda_q + i\omega_q)t}$ and $G_q^* e^{(-\lambda_q - i\omega_q)t}$ together make a contribution to $G_2(t)$ of relative magnitude $2|G_q|$ in a term $2|G_q| e^{-\lambda_q t} \cos(\omega_q t + \varphi_q)$, where $\tan \varphi_q = \text{Im } G_q / \text{Re } G_q$.

We use $1/\omega_{Qf}$ as the time scale, where ω_{Qf} is the quadrupole frequency of the fluctuating part of the efg. ω_{Qs} is the quadrupole frequency of the static part of the efg, so $\gamma = \omega_{Qs}/\omega_{Qf}$. The frequencies and relaxation rates for which G_q is large enough to make at least a 2% contribution to $G_2(t)$ are shown versus $\log(w/\omega_{Qf})$ in figs. 1-3 for $\gamma = 0, 0.01$, and 1.

With the frequencies, relaxation rates, and coefficients G_q from an accurate computer calculation, one can immediately generate $G_2(t)$ using eq. (2). G_2 is shown as a function of t and w in figs. 4-6 for $\gamma = 0, 0.01$, and 1. Note the progression from static patterns at small w to exponential relaxation for large w in the $\gamma = 0$ case. For $\gamma = 0.01$ one sees the very low frequency static efg pattern at large w on a sufficiently long time scale. For $\gamma = 1$ the frequencies associated with the three efg states of the model are evident for all w except $1 < w < 10$. We have not shown figures for large γ because they simply reflect the static patterns, with relaxation having decreasing effects as γ increases. As discussed below, $G_2(t)$ can often be approximated over a wide range of w and γ by relatively simple functions that are convenient for fitting PAC spectra.

A. Slow Fluctuation (Low Temperature) Case: $w < \omega_{Qf}$

For small w the frequencies ω_i are the static frequencies for the three efgs of the model.

For $\gamma \neq 0$, one has an axially symmetric state with V_{zz} proportional to $(1 + \gamma)$ (axes of static and fluctuating parts both aligned along z) and two nonaxial states (axes of static and fluctuating parts orthogonal). Since the frequencies remain reasonably constant, and the relaxation rates vary as w , relatively simple approximations for $G_2(t)$ should hold when $w < \omega_{Qf}$, as observed previously for similar, but more symmetric models by Baudry and Boyer [3]. However, the γ -dependence of these models is somewhat complicated, so we resort to fitting to a heuristic form that does well for some appropriate range of w and γ . When $w < 0.1\omega_{Qf}$ we have the especially simple form

$$G_2(t) \cong \frac{1}{3}e^{-\lambda_z t}G'_{2z}(t) + \frac{2}{3}e^{-\lambda_{xy} t}G'_{2xy}(t), \quad (5)$$

where

$$\begin{aligned} G_{2z}(t) = & S_0(0) + S_1(0) \cos 6(1 + \gamma)\omega_{Qf}t + S_2(0) \cos 12(1 + \gamma)\omega_{Qf}t \\ & + S_3(0) \cos 18(1 + \gamma)\omega_{Qf}t, \end{aligned} \quad (6)$$

and

$$\begin{aligned} G_{2xy}(t) = & S_0(\eta) + S_1(\eta) \cos \omega_1(\eta)t + S_2(\eta) \cos \omega_2(\eta)t \\ & + S_3(\eta) \cos \omega_3(\eta)t. \end{aligned} \quad (7)$$

Here

$$\gamma = \begin{cases} 3\gamma/(2 - \gamma) & 0 \leq \gamma \leq 0.5, \\ |1 - \gamma|/(1 + \gamma) & 0.5 \leq \gamma \leq 2, \\ 3/(2\gamma + 1) & \gamma \geq 2. \end{cases} \quad (8)$$

$S_n(\eta)$ and $\omega_n(\eta)$ are the usual static $I = \frac{5}{2}$ electric quadrupole PAC coefficients and frequencies for asymmetry η . It is convenient to define a dimensionless quantity ζ to express the γ -dependence of the quadrupole frequency to be used in calculating $\omega_n(\eta)$. Then this quadrupole frequency is given by $\omega_Q(\gamma) = \zeta\omega_{Qf}$, where

$$\zeta = \begin{cases} 1 - \frac{1}{2}\gamma & 0 \leq \gamma \leq 0.5, \\ \frac{1}{2}(1 + \gamma) & 0.5 \leq \gamma \leq 2, \\ \gamma - \frac{1}{2} & \gamma \geq 2. \end{cases} \quad (9)$$

Best fits for the effective λ_z and λ_{xy} are shown in fig. 7. These fits were obtained by assuming a standard deviation in $G_2(t)$ at $t = 0$ of 0.5% and increasing the uncertainty with time as appropriate for good experimental data. The fits were performed over three periods of the fluctuating efg oscillations, i.e. $t = 0$ to π/ω_{Qf} . The probe intermediate state mean lifetime was assumed to be approximately equal to $\pi/3\omega_{Qf}$, one PAC period. χ^2 per degree of freedom was $\ll 1$ for most values of γ , exceeding 1 and reaching to a maximum of 5 when $w = 0.1\omega_{Qf}$ with $\gamma > 2$.

Eqs. (5-9) provide a reasonable approximation for all γ if $w < 0.1\omega_{Qf}$. When $0.1\omega_{Qf} < w < \omega_{Qf}$, equally simple forms for $G_2(t)$ can be found, but the parameters depend on γ in a more complicated way. If γ is known from experiment or for a particular physical model of interest, then it is straight-forward to express $G_2(t)$ in terms of a small number of

parameters. The high symmetry of the model considered by Baudry and Boyer[3] leads to a wider range of validity for their simple approximate form than is the case here. However, in all these models we expect the frequencies and phases of the approximate form to deviate from those of the underlying static efgs when $w > 0.1\omega_{Qf}$. Therefore, one must carefully connect the fitted parameters to the model in order to see clearly the physics of the defects.

B. Rapid Fluctuation (High Temperature) Case ($\gamma > 0$):

In the rapid fluctuation regime, $w > \max(10\omega_{Qf}/\gamma, 20\gamma\omega_{Qf})$, the frequencies due to the very rapidly fluctuating efgs are not seen (their average is zero), and only the static part of the efg remains. Unlike the slow fluctuation case, where heuristic expressions are needed, we have an exact expression for $G_2(t)$ in the rapid fluctuation limit. This expression, which includes several exponentials, is more complicated than the approximate forms used in the slow fluctuation case and that proposed by Baudry and Boyer [3] in this limit. However, it is exact (for $N = 3$) in the limit of rapid fluctuations, and it has no more independent parameters than the heuristic forms, so is therefore as convenient to use for fitting experimental data.

As is well known, the relaxation rate is proportional to $1/w$ in this case [4]. Winkler and Gerdau [2] showed that for large w the XYZ model relaxation approaches the Abragam-Pound expression, $\lambda_{AP} = 100.8\omega_{Qf}^2/Nw$, where $N = 3$ for the XYZ+Z family of models. More generally, their derivation shows for large w in the XYZ model that

$$\sum_q G_q \lambda_q = \lambda_{AP}. \quad (10)$$

When $\gamma \neq 0$, as here, we have shown analytically [10] that the large w limit of the XYZ+Z model yields

$$\sum_q G_q \lambda_q = \frac{107}{98} \lambda_{AP}. \quad (11)$$

We find the relatively simple approximate form (which is exact in the rapid limit) for $G_2(t)$:

$$G_2(t) = 0.131 e^{-\lambda_0 t} + 0.069 e^{-\lambda'_0 t} + \frac{13}{35} e^{-\lambda_1 t} \cos 6\gamma \omega_{Qf} t + \frac{2}{7} e^{-\lambda_2 t} \cos 12\gamma \omega_{Qf} t + \frac{1}{7} e^{-\lambda_3 t} \cos 18\gamma \omega_{Qf} t, \quad (12)$$

where $\lambda_n = \alpha_n \omega_{Qf}^2 / w$ with $\alpha_0 = 12.38$, $\alpha'_0 = 13.62$, $\alpha_1 = 29$, $\alpha_2 = 38$, and $\alpha_3 = 73$. In addition to the sum rule of eq. (11), we have shown analytically [10] that

$$0.131 \lambda_0 + 0.069 \lambda'_0 = \frac{27}{196} \lambda_{AP};$$

$$\lambda_1 = \frac{145}{168} \lambda_{AP}; \quad \lambda_2 = \frac{285}{252} \lambda_{AP}; \quad \lambda_3 = \frac{365}{168} \lambda_{AP}. \quad (13)$$

C. Intermediate Fluctuation Case:

One finds maximum relaxation at intermediate fluctuation rates in the range

$\omega_{Qf} < w < 10\omega_{Qf} \times \max(1, \gamma)$. In this region the crossover from slow to rapid fluctuations

gives a complicated $G_2(t)$ which is not easily represented by functions of w and γ as in the previous two cases.

However, if γ is small enough, there is a part of the intermediate region for which $20\omega_{Qf} < w < \omega_{Qf}/\gamma$. In this range, the XYZ+Z model reduces to the rapid fluctuation limit of the XYZ model [10], i.e.

$$G_2(t) = 0.3032e^{-10.15\omega_{Qf}^2 t/w} + \frac{4}{7}e^{-38\omega_{Qf}^2 t/w} + 0.0968e^{-63.85\omega_{Qf}^2 t/w} + \frac{1}{35}e^{-92\omega_{Qf}^2 t/w} \quad (14)$$

Once again, this expression is complicated by being a sum of several exponentials.

However, it is exact (for $N = 3$) in this limit, as was eq. (12).

IV. APPLICATIONS

A. Tetragonal Zirconia

Zirconia (ZrO_2) doped with yttria (Y_2O_3) forms a solid of monoclinic, tetragonal, or cubic symmetry, depending on doping. The yttria dopant introduces yttrium substitutions at zirconium sites and one-half oxygen vacancy for each yttrium. The yttrium substitutions plus the crystal field in the tetragonal phase introduce a small, axially symmetric efg that, for a very wide range of temperature, is static on the time scale of tens of nanoseconds, *i.e.* the time scale of the intermediate state of the PAC probe. The oxygen vacancies are trapped near the ^{111}Cd probe [11,12]. They apparently hop around the probe in the trapping shell and produce a much larger efg that fluctuates, mostly in direction. The trapped vacancies thus contribute an approximately axially symmetric efg which fluctuates

at the rate of the vacancy jumps so w is activated and reflects the hopping barrier height.

The physics of this system is embodied in the XYZ+Z model with $\gamma < 1$. We have obtained excellent fits to the data in the rapid fluctuation regime using the $\gamma = 0.01$ model [7,12], as shown in fig. 8. This model, with an additional simple statistical mechanics model for the trapping probability as a function of dopant concentration, then allows the determination of the hopping energy around the probe trap and the trap energy. Based on some simple physical assumptions one finds $E_h = 0.8 \pm 0.05$ eV and $E_A = 0.44 \pm 0.05$ eV, respectively.

B. Undoped Ceria

Undoped ceria (CeO_2) has a cubic structure, so there is no static efg contributed by the lattice. However, there are small amounts of oxygen vacancies, due to trace impurities, in the 50 to 100 ppm range. These vacancies are trapped by the ^{111}Cd probe, and the primary contribution to the efg at the probe nucleus is from the trapped vacancy [11,13].

This system reflects the XYZ model, i.e. $\gamma = 0$. As shown in fig. 9, the spectra have the form predicted by this model for a wide range of temperatures. At low temperature one sees a static spectrum which gradually changes to exponential decay. The relaxation rate increases to a peak near 300°C and then decreases. A full report of this work, including fits of the physical parameters, is in preparation [13].

V. CONCLUSIONS

The three fluctuation rate regimes can be understood by examining more closely the

relationships between w , ω_{Qf} , and γ in each case. The slow fluctuation case is that for which the fluctuation rate, w , is small compared to the quadrupole frequency of the various efgs in the model. Therefore, the quadrupole interaction dominates in this regime, and we see the static frequencies of all the efgs, with relaxation increasing proportionally to w as fluctuations increase.

The rapid fluctuation case is that for which $w > \omega_{Qf}/\gamma$, i.e. $\omega_{Qs} > \omega_{Qf}^2/w$. The relaxation rate in the rapid fluctuation regime is proportional to ω_{Qf}^2/w [4]. So in this case, the static part of the quadrupole interaction dominates, and we see the frequencies associated with that part of the efg. Nuclear relaxation damps out the static efg oscillations as shown in eq. (12).

The small- γ intermediate fluctuation case is that for which w is large compared to ω_{Qf} , i.e. relaxation dominates the fluctuating efgs. However, $\omega_{Qs} < \omega_{Qf}^2/w$. Hence, the relaxation also dominates the static efg in this case, and one sees multiple exponential decay as in eq. (14).

The frequencies which appear in $G_2(t)$ for a given γ are easily understood. For w in the slow or rapid fluctuation regimes, they are approximately constant and equal to the static frequencies of the three efgs of the model for small w or the frequencies of the static efg alone for large w . For small w , an asymmetry is introduced by adding a fluctuating, axially symmetric efg to a static, axially symmetric efg with symmetry axes orthogonal to one another.

In both the rapid and slow fluctuation regimes several different exponentials contribute to

the relaxation. This is expected from the work of Andrade *et al.* [6] and that of Dillenburg and Maris [14]. Andrade *et al.* found several relaxation rates in models in which the fluctuating efg is much smaller than the static efg. Dillenburg and Maris showed that fluctuations too large to be treated in first-order perturbation theory lead to two exponentials for rapid fluctuations in the $I = \frac{5}{2}$ case.

The relaxation rates for rapid or small- γ intermediate fluctuations are related to the Abragam-Pound relaxation rate by sum rules. The sum rule for the small- γ intermediate regime of the XYZ+Z model and the rapid limit of the XYZ model is given by eq. (10). That for the XYZ+Z rapid limit is given by eqs. (11) and (13) above.

In practice, it is important to know when one needs to use the expressions for $G_2(t)$ given above rather than the simpler expressions given by Baudry and Boyer [3]. The object of PAC experiments is not simply to measure hyperfine parameters of spectra but to extract physical information from the spectra. For moving defects in solids which can be described by the XYZ+Z family of models, that information is contained in the parameters w , ω_{Qf} , ω_{Qs} , and their temperature and dopant concentration dependences. If one can measure a sufficiently wide temperature range to see both ω_{Qf} (at low temperatures) and ω_{Qs} (at high temperatures) with a smooth transition in between which gives $w(T)$ from the relaxation, then the expressions given here may be necessary to obtain consistent fits to the physical parameters over the whole range. On the other hand, in many practical situations an approximation which combines the various exponentials using only their linear expansions be adequate. However, whenever using approximate forms to fit PAC spectra one must be very careful to connect the fitting parameters correctly to the model

parameters in order to understand the physics of the defects.

The XYZ+Z family allows fitting of PAC data over a wide range of temperatures and dopant concentrations in a physically meaningful way within the framework of a single model. Thus, one can extract physical properties of defects in materials with confidence because many spectra can be fitted consistently by a single physical model.

VI. ACKNOWLEDGMENTS

We are grateful to Ms. Ashley Schultz, Mr. Brian Busse, and Mr. Andrew Evenson for technical assistance. We acknowledge helpful conversations with Professor Henri Jansen. This work was supported in part by the US DOE under contract DE-FG06-85ER45191.

FIGURES

Fig. 1. XYZ model: (a) frequencies (ω_q/ω_{Qf}) and (b) relaxation rates (λ_q/ω_{Qf}) which contribute at least 2% to $G_2(t)$ as a function of efg fluctuation rate (*i.e.* defect jump rate).

Fig. 2. XYZ+Z model with static efg 1% of the fluctuating efg: (a) frequencies (ω_q/ω_{Qf}) and (b) relaxation rates (λ_q/ω_{Qf}) which contribute at least 2% to $G_2(t)$ as a function of efg fluctuation rate.

Fig. 3. XYZ+Z model with static efg equal to the fluctuating efg: (a) frequencies (ω_q/ω_{Qf}) and (b) relaxation rates (λ_q/ω_{Qf}) which contribute at least 2% to $G_2(t)$ as a function of efg fluctuation rate.

Fig. 4. XYZ model: $-G_2$ as a function of t and w .

Fig. 5. XYZ+Z model with static efg 1% of the fluctuating efg: $-G_2$ as a function of t and w .

Fig. 6. XYZ+Z model with static efg equal to the fluctuating efg: $-G_2$ as a function of t and w .

Fig. 7. Best fits for (a) λ_z/w and (b) λ_{xy}/w as a function of γ for the slow fluctuation regime. The lines are guides to the eye. The error bars are those appropriate for $w = 0.1$.

Fig. 8. A_2G_2 PAC spectra for ^{111}Cd in 0.2 at.% yttria-doped tetragonal zirconia. Both frequencies and relaxation change with temperature due to the temperature dependence of the oxygen vacancy jump rate and of the Cd -oxygen vacancy trapping probability. The

lines are fits with the $\gamma = 0.01$ XYZ+Z model.

Fig. 9. A_2G_2 PAC spectra for ^{111}Cd in undoped ceria for various temperatures. The lines are fits with the XYZ model.

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XYZ Model ($\gamma = 0.0$)

XYZZ Model, $\gamma = 0.01$

XYZZ Model, $\gamma = 1.0$

XYZ MODEL ($\gamma = 0$)

XYZ+Z MODEL: $\gamma = 0.01$

END

DATE FILMED

02 / 01 / 91