RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 34, NUMBER 12 15 DECEMBER 1986

Electric field gradients of randomly disordered compounds

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(Received 2 July 1986)

The distribution of the electric-field-gradient tensor parameters is evaluated for a randomly disordered structure displaying an intrinsic local symmetry. The second-order symmetries of the nonperturbed system are defined by the two central parameters Δ_0 and η_0; then the corresponding distribution in the disordered modification is governed by one order parameter $\lambda = \Delta_0/\sigma$ where σ^2 is the variance in the components of the perturbing tensor. An approximate analytical expression is proposed with the purpose of interpreting experimental data in terms of relevant structural parameters for compounds where the local symmetry is randomly disturbed, e.g., quasicrystals, amorphous alloys, or disordered rare-earth compounds with a symmetry lower than cubic. It should be emphasized that the intrinsic parameters characterizing the underlying symmetry (Δ_0, η_0) are significantly different from the corresponding mean values of the distribution, as soon as the disorder becomes finite.

The modeling of disordered structures without long-range periodicity like amorphous and quasicrystalline materials, implies the knowledge of not only pair correlation functions (as deduced from scattering experiments) but also of the correlation functions that involve more than two atomic positions. Therefore, the local symmetry properties provide an important insight into the puzzle of these high-order correlations. These symmetries are reflected by multipolar fields (crystalline electric fields).[1] In particular, the second-order crystal fields (B_2^0, B_2^2) acting at rare-earth atoms[2] or the electric-field-gradient tensor (EFGT) at the nucleus of S-state ions are direct probes of the second-order symmetries, i.e., of the three- and four-atom correlation functions.[1,3]

There is an increasing amount of evidence that the amorphous order possesses the characteristics of some underlying crystal phase.[4-6] On the other hand, in order to test models of decoration for quasicrystalline lattices, it is crucial to determine whether these phases have an intrinsic point symmetry lower than cubic (and in turn lower than icosahedral) phases or whether the measured EFGT only arises from fluctuations due to the lack of periodicity.[7,8] Hence, it is of primary importance to predict the EFGT distribution for a randomly perturbed structure showing an intrinsic second-order symmetry, i.e., $\Delta_0 \neq 0$. With the help of numerical simulations, an approximate analytical expression is derived which should be very useful to analyze quadrupolar interaction data.

Let V_{ik} be the components of the 3×3 EFG tensor $[V]$. $[V]$ being symmetric and traceless is fully determined by five independent quantities, e.g., three Euler angles (α,β,γ) and two components of the trace in the eigenframe, i.e., the principal component V_{zz} and the asymmetry parameter $\eta = |V_{xx} - V_{yy}|/|V_{zz}|$. In the presence of a distribution of the eigenvalues of $[V]$, a polar coordinate representation (Δ,ϕ) is more convenient since it avoids the unphysical discontinuities that are introduced by the definition of V_{zz} and η.[9] The following results can also be straightforwardly applied to rare-earth compounds, recalling that $B_2^0 \propto V_{zz}$ and $|B_2^2/B_2^0| = \eta$.[2] By defining the two real invariants S and D (Ref. 3) as

$$S = \tfrac{2}{3}\sum_{i=1}^{3} V_{ik}^2 = V_{zz}^2(1+\eta^2/3) \ ,$$
$$D = 4\det[V] = V_{zz}^3(1-\eta^2) \ , \qquad (1)$$

then one has

$$\Delta = S^{1/2} \ ,$$
$$\phi = \tfrac{1}{3}\sin^{-1}(D/\Delta^3) \ . \qquad (2)$$

In a disordered macroscopic sample, an overall isotropy is expected, i.e., a distribution $P(\Delta,\phi)$ that is invariant under any rotation. This assumption implies drastic constraints on the distributions of the components of $[V]$ as well as on the correlations between them.[10-13] Independent V_{ik} variables imply that each of the V_{ik} is normally distributed.[12] This particular situation is found in randomly disordered structures, where there is *a priori* no intrinsic second-order symmetry like, e.g., the dense random packing of spheres[3] or a cubic lattice with random point defects.[14] A noncubic symmetry implies quadratic and cubic correlations between the V_{ik}'s resulting from restrictions over the variations of S and D, as well as non-normal distributions. Notice that linear correlations between normally distributed V_{ik}'s do not fulfill rotational invariance.[13,15] In this work, the distribution of the V_{ik}'s is generated by assuming that

$$[V] = [T] + [\varepsilon] \ , \qquad (3)$$

where $[T]$ is a fixed strength tensor[12] that describes the nonperturbed structure. The distribution of the real invariants of $[T]$ are Dirac δ functions corresponding to $\Delta = \Delta_0$ and $\phi = \phi_0$.

The randomly perturbing tensor $[\varepsilon]$ is assumed to have independent normally distributed components:

$$P(\varepsilon_{ij}) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left[-\frac{\varepsilon_{ij}^2}{2\sigma^2} \right] . \quad (4)$$

These two tensors as well as their sum [Eq. (3)] obviously satisfy rotational invariance.[12] It is natural to define the noncentrality parameter λ (or order parameter) by

$$\lambda = \Delta_0/\sigma . \quad (5)$$

The reduced quadrupole splitting of the tensor $[V]$ is defined by $\delta = \Delta/\sigma$; then the distribution $P_0(\delta,\phi)$ for $\lambda=0$ is given by[3,9]

$$P_0(\delta,\phi) = \frac{\cos(3\phi)}{\sqrt{2\pi}\sigma} \delta^n \exp\left[-\frac{\delta^2}{2} \right] , \quad (6)$$

where $n+1=5$ is the number of degrees of freedom. No simple analytical expression can be found for $P(\delta,\phi)$ when $\lambda \neq 0$. However, the marginal distribution of δ, i.e., $Q(\delta)$ has still an analytical form, being derived from a noncentral χ^2 distribution with five degrees of freedom:[4,13,16]

$$Q(\delta) \propto \delta g(\delta\lambda) \exp[-\tfrac{1}{2}(\delta-\lambda)^2] , \quad (7)$$

where $g(x)=(x-1)+(x+1)\exp(-2x)$. One can easily deduce that when $x \simeq 0$, i.e., when $\Delta\Delta_0/\sigma^2 \ll 1$, the preexponential factor $\delta g(\delta\lambda)$ is proportional to Δ^4, whereas in the limits of $\Delta\Delta_0/\sigma^2 \gg 1$, it is equivalent to Δ^2. It is worth noticing that an effective power n^* of δ in Eq. (6) verifying $2<n^*<4$ (Ref. 7) is a signature of $\lambda \neq 0$, i.e., of a noncubic intrinsic symmetry.

With the aim to study the marginal distribution of ϕ, i.e., $R(\phi)$ and the possible correlations between δ and ϕ, numerical simulations were undertaken, using Eqs. (1)–(5) for various values of λ and η_0. The tensor $[T]$ was rotated in all directions with proper weighting factors. Independent normal distributions were generated by a Monte Carlo method[17] over $\sim 2^{19}$ iterations. The accuracy of the simulated distributions was successfully checked against the above given analytical expressions for $\lambda=0$ [Eq. (6)] and $\lambda \neq 0$ [Eq. (7)].

A first series of simulations was done for $\eta_0=1$ ($\phi_0=0$); indeed, owing to parity arguments, no linear correlation is then expected between δ and ϕ. At small values of λ, $R(\phi)$ is largely dominated by the $\cos(3\phi)$ term of Eq. (6), which is the consequence of the Jacobian of the transformation from the V_{ik} components to δ and ϕ.[3] To illustrate this behavior, the simulated marginal distribution $R(\phi)$ divided by $\cos(3\phi)$ is shown in Fig. 1 for various values of λ. By fitting of the simulated curves, it has been found that, to a very good accuracy, $R(\phi)_{\eta_0=1}$ can be approximated by

$$R(\phi)_{\eta_0=1} \simeq \cos(3\phi) \exp\left[-\frac{(\phi-\phi_0)^2}{2\sigma_\phi^2} \right] \text{ for } -\pi/6 \le \phi \le \pi/6 , \quad (8)$$

with $\phi_0=0$ and σ_ϕ a function of λ, as shown in Fig. 2. It is remarkable that, for values of λ larger than $\simeq 7$, $\sigma \simeq 1.18/\lambda$ (ϕ and σ_ϕ being expressed in radians). On the other hand, for $\lambda \le 5$, i.e., $\sigma_\phi \ge 0.26$, the departure of $R(\phi)$ from a pure $\cos(3\phi)$ curve is negligible and is expected to escape to experimental investigations by Mössbauer or NMR spectroscopies.

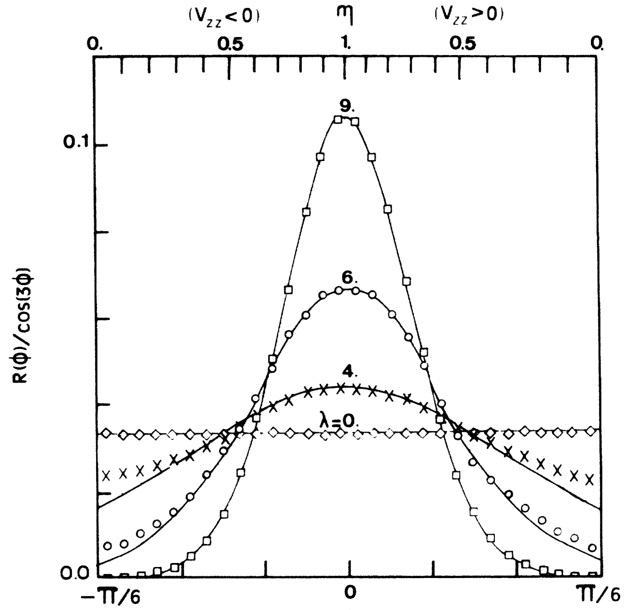

FIG. 1. Plot of the marginal distribution $R(\phi)$ divided by $\cos(3\phi)$ for $\eta_0=1$ ($\phi_0=0$) and for several values of $\lambda=\Delta_0/\sigma$. Values of η are reported in the upper scale, including also the sign of V_{zz}.

The situation becomes more complicated when $\eta_0 \neq 1$, i.e., $\phi_0 \neq 0$. A very remarkable feature is that, whatever the values of λ and ϕ_0, $R(\phi)$ is always linearly vanishing at $\phi = \pm\pi/6$. This means that an axial symmetry is unstable with respect to any finite random perturbation, similarly to the cubic symmetry. This behavior, can be directly deduced by adapting a result of Rozenzweig[18] in the limit $\lambda \gg 1$. Let $d\theta_i$ be the small difference between the three respective eigenvalues ($i=1,2,3$) of $[V]$ and $[T]$; one has

$$\prod_{i=1}^{3} d\theta_i \eta_0 (1-\eta_0^2/9) V_{zz_0}^3 = k \prod_{\substack{i,k=1 \\ (i<k)}}^{3} \varepsilon_{ik} , \quad (9)$$

where $k \simeq 0.66$.

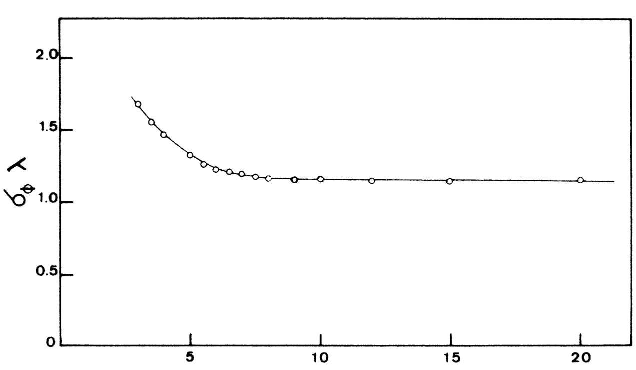

FIG. 2. Plot of σ_ϕ/λ vs λ.

An examination of the computed $P(\delta,\phi)_{\eta_0,\lambda}$ distribution functions leads to the conclusion that the correlation between δ and ϕ remains negligible (less than 0.04) when $\eta_0 \geq 0.75$. Then $R(\phi)_{\eta_0,\lambda}$ is still well approximated by Eq. (8), where the central value ϕ_0 is deduced from η_0 and from the sign of V_{zz_0} through Eqs. (1) and (2). Similarly, to the case $\eta_0 = 1$, a modified marginal distribution $R(\phi)/\cos(3\phi)$ has been numerically calculated for various values of λ and η_0. This modified distribution has still a nearly Gaussian shape centered at ϕ_0; the value of σ_ϕ is the same function of λ as for $\eta_0 = 1$.

When the underlying symmetry approaches axial symmetry, then a significant correlation appears between δ and ϕ (Figs. 3 and 4). With the aim to simplify the final analytical expression for $P(\delta,\phi)$, a correlation coefficient is included in the Gaussian part of $P(\delta,\phi)$. ρ is evaluated numerically from the transformed distribution $P'(\delta,\phi) = P(\delta,\phi)/\cos(3\phi)g(\delta\lambda)\delta$ which is approximately a 2D normal distribution. Values of ρ are reported for various values of η_0 and λ in Fig. 5. Then, for any value of λ and η_0 it is possible to approximate the distribution function of δ and ϕ with the following formula:

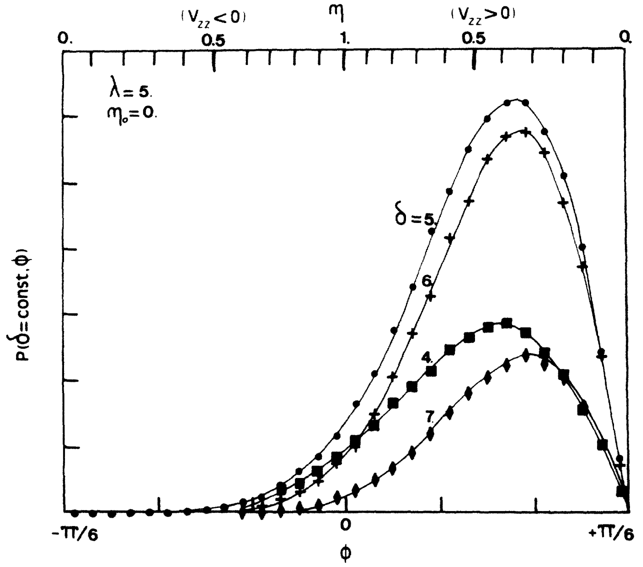

FIG. 3. Plot of $P(\delta,\phi)$ at several constant values of δ, and for $\lambda = 5$ and $\eta_0 = 0$.

$$P(\delta,\phi) \simeq \delta g(\delta\lambda)\cos(3\phi)\exp\left\{-\frac{1}{2(1-\rho^2)}\left[(\delta-\lambda)^2+\left(\frac{\phi-\phi_0}{\sigma_\phi}\right)^2+\frac{\rho(\delta-\lambda)(\phi-\phi_0)}{\sigma_\phi}\right]\right\}, \tag{10}$$

where $g(x)$ is given by Eq. (7), ϕ and ϕ_0 are related with η and η_0, respectively, by Eqs. (1) and (2), σ_ϕ and ρ are given in Figs. 2 and 5.

In summary, an approximated analytical formula is proposed with the aim of constructing the combined distribution of the two real parameters Δ and ϕ (or η) that describe the electric field gradient in a randomly perturbed structure, showing an intrinsic symmetry given by Δ_0 and ϕ_0 (η_0). With help of a seminumerical approach, it has been found that the marginal distribution of ϕ always linearly vanishes when $\phi = \pm\pi/6$ (i.e., $\eta = 0$). This result is particularly important with respect to disordered rare-earth compounds. Indeed, the uniaxial anisotropy ($B_2^2 = 0$), i.e., $\phi = \pm\pi/6$, is fully destroyed by any finite random perturbation of the crystal field. The restriction of the crystal-field Hamiltonian to the second-order uniaxial term ($B_2^0 \neq 0$, all other terms $\equiv 0$) in random anisotropy models[19] could fail in describing disordered compound (amorphous, dilute Y-base alloys, etc.). A significant correlation is found between ϕ and Δ, especially when the underlying symmetry is close to axial ($\eta_0 \simeq 0$). The proposed formula should permit one to analyze experimental

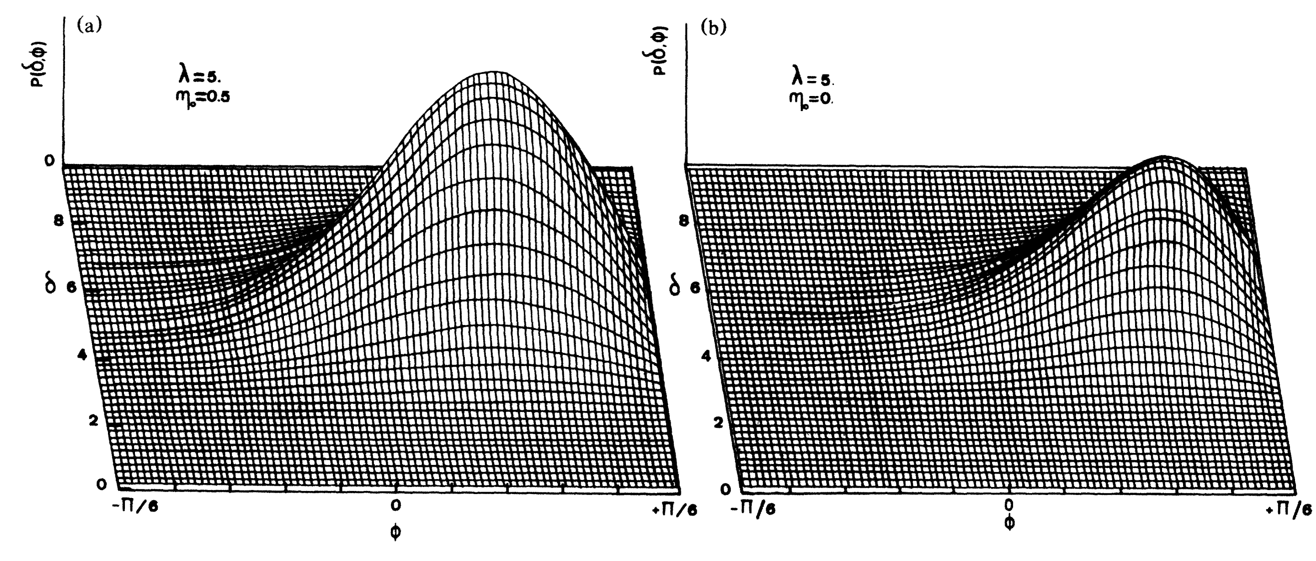

FIG. 4. Distribution function $P(\delta,\phi)$ numerically computed for $\lambda = 5$ and (a) $\phi_0 = 0.281$ ($\eta_0 = 0.5$) or (b) $\phi_0 = +\pi/6$ ($\eta_0 = 0$). Both cases correspond to $V_{zz_0} > 0$.

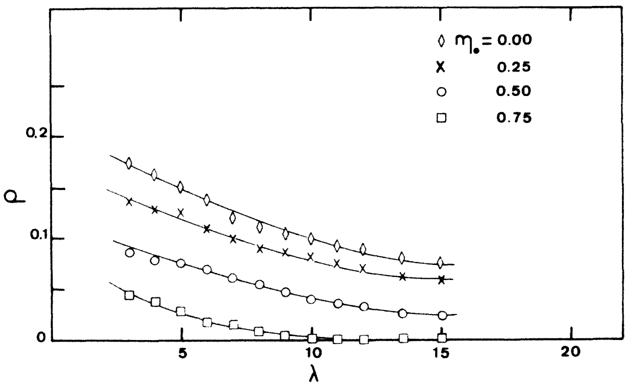

FIG. 5. Plot of the correlation coefficient ρ as a function of λ and for several values of $\eta_0(\phi_0>0)$. The opposite value of ρ is found when ϕ_0 is changed into $-\phi_0$.

data of the electric-field-gradient distribution or of second-order crystal-field distributions with help of only one order parameter $\lambda=\Delta_0/\sigma$. Additionally, it will help to determine whether the intrinsic symmetry of probe atoms in Al-Mn or Pd-U-Si quasicrystals is lower than icosahedral ($\Delta_0\neq 0$). This point is crucial for testing decoration models of the quasilattice. Extensive analysis of in-field Mössbauer data of amorphous alloys is now in progress using the above formalism.[20]

I gratefully thank Professor J. A. Mydosh for his hospitality during my stay in the Kamerlingh Onnes Laboratorium. I am also indebted to all the members of the Metal Physics group for their fruitful discussions. Financial support from the Centre National de la Recherche Scientifique (France) is acknowledged.

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