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Distribution of electric field gradients in decagonal quasicrystals

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Abstract

We measured the orientation dependent ^{27}Al NMR spectra of a decagonal Al-Ni-Co quasicrystal. In order to explain the experimental results, we had to introduce a model of EFGs in decagonal quasicrystals. The EFGs reflect the structure of quasicrystals. Therefore, from the comparison between the NMR results and the models of EFGs, we can test the atomic structure models of quasicrystals.

Keywords: Electric field gradient; Nuclear magnetic resonance; Spectrum; Quasicrystals;

1 Introduction

Whereas in the last twenty years nuclear magnetic resonance (NMR) was successfully used in the field of quasicrystals on getting insight into the electronic structure and magnetism [1,2] and, on the other hand, into excitations, fluctuations and diffusion [3,4], no breakthrough has been achieved by NMR in determining the atomic structure of the quasicrystals. NMR spectroscopy is a very useful experimental tool for getting information about the local chemical environments. The dominant nuclear spin interaction that determines the ^{27}Al NMR lineshape of Al-based quasicrystals is the electric quadrupolar interaction, which reflects the structure of the quasicrystals through the distribution of the electric field gradients (EFGs). From pioneering work on icosahedral quasicrystals [5], we know that the NMR spectrum is determined by a wide distribution of EFG tensors reflecting a high number of inequivalent lattice sites, in agreement with quasiperiodic structure. This is the case also for 2D quasicrystals, which consist of periodic stacks of quasiperiodic layers of atoms along the twelve-, ten- or eightfold rotational symmetry axis. In the following section, the NMR measurements on decagonal Al-Ni-Co quasicrystal are briefly presented [6], whereas the last section is devoted to a simple model of EFG distribution in 2D quasicrystals. In this work we further evolve a “stacked planar” model firstly introduced in Ref. [6].

2 Orientation dependent ^{27}Al NMR spectra of decagonal Al-Ni-Co quasicrystal

The NMR resonance frequency corresponding to the $m \leftrightarrow m-1$ spin transition of the i th ^{27}Al nucleus with spin $I = 5/2$ can be written as a sum [5,7]

$$\nu_i(m \leftrightarrow m-1) - \nu_0 = \nu_{quad,i}^{(1)}(m \leftrightarrow m-1) + \nu_{quad,i}^{(2)}\left(\frac{1}{2} \leftrightarrow -\frac{1}{2}\right) + \nu_{mag,i}, \quad (1)$$

where $\nu_0 = \gamma_n B_0 / 2\pi$ is the Zeeman frequency in the external magnetic field B_0 and γ_n is the nuclear gyromagnetic ratio. The first term $\nu_{quad,i}^{(1)}$ on the right of equation (1) is the first-order quadrupole shift

that affects any spin transition $m \leftrightarrow m-1$ except the central one (these transitions are also called satellite transitions) and is independent of the external magnetic field B_0 . It can be written in the following form [8]

$$\nu_{quad,i}^{(1)}(m \leftrightarrow m-1) = -\frac{V_{Q,i}}{2} \left(m - \frac{1}{2}\right) \left(3 \cos^2 \theta_i - 1 + \eta_i \sin^2 \theta_i \cos 2\phi_i\right). \quad (2)$$

Here the angles θ_i and ϕ_i define the orientation of the external field B_0 with respect to the EFG tensor principal-axes system. The quadrupole coupling constant of the i th spin $I = 5/2$ nucleus $\nu_{Q,i} = 3eV_{ZZ,i}Q/20h$ is determined by the largest eigenvalue of the EFG tensor $V_{ZZ,i}$, whereas $\eta_i = (V_{XX,i} - V_{YY,i})/V_{ZZ,i}$ is the quadrupole asymmetry parameter. The second term $\nu_{quad,i}^{(2)}$ represents the quadrupolar shift in the second-order of perturbation that is dominant only on the central transition $\frac{1}{2} \leftrightarrow -\frac{1}{2}$, which is not affected by the first-order quadrupolar interaction. Finally, the last term $\nu_{mag,i}$ corresponds to the frequency shift due to magnetic hyperfine coupling between the nuclear spins and the s , p and d conduction electrons. The experiment has shown that we actually need to include only isotropic part of the magnetic interaction that can be simplified into a uniform site-independent Knight shift [5,6]. In summary, we see that the NMR spectrum of the quasicrystals is predominantly determined by the distribution of the EFG parameters $g(\nu_Q, \eta, \theta, \phi)$ that reflect the atomic structure. The angular dependence of the NMR spectrum is introduced through the anisotropic distribution of the parameters θ in ϕ .

[Insert Figure 1 about here.]

The NMR measurements were performed on a decagonal $\text{Al}_{72.6}\text{Ni}_{10.5}\text{Co}_{16.9}$ single-grain quasicrystal grown by the flux technique. The sample was rotated about the twofold and tenfold axes. For the tenfold rotation, a weak angular dependence of the NMR spectrum was expected with the $2\pi/10$ period, since in this case the magnetic field rotates within the quasiperiodic plane with the tenfold symmetry. On the other hand, for rotation about the twofold axis, a strong angular dependence was expected, while here the tenfold axis changes its orientation relative to the field. The experiment confirmed our predictions, as for twofold rotation a strong angular dependence was observed for satellite part of the ^{27}Al NMR spectrum (Figure 1 a)) as well as for the central line (Figure 1 b)). This is also evident from the strong angular dependence of the center of gravity of the ^{27}Al central line, the so-called first moment M_1 , as shown in Figure 1 c). Besides, a tiny angular dependence of the first moment M_1 was also detected for rotation about the tenfold axis as displayed in Figure 1 d). Nevertheless, the quasiperiodic symmetry $2\pi/10$ is clearly visible. For more details on the NMR techniques employed, see Refs. [6,9].

3 Simple model of EFG distribution in 2D quasicrystals

In our search for a model of EFG distribution in the decagonal Al-Ni-Co quasicrystals, we first revisited the icosahedral Al-Pd-Mn quasicrystals. The EFG distribution, which can satisfactorily reproduce the observed NMR spectrum of icosahedral quasicrystals [9], can be numerically simulated by a dense random packing of hard spheres (Figure 2 a)) using the point-charge model [10], known as

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4 the spherically isotropic Czjzek model [11]. Here one has to keep in mind that the adequacy of this
5 model has its limitation because even in icosahedral quasicrystals, a tiny angular dependence was
6 observed [12]. Actually, this weak anisotropy can be explained in the frame of the Czjzek model with
7 equal $P(v_Q, \eta)$ distribution but slightly modified anisotropic angular distribution $S(\theta, \phi)$ obeying the
8 icosahedral symmetry [13].
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12 [Insert Figure 2 about here.]
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15 In analogy to the icosahedral case, a simple model of EFG distribution in 2D quasicrystals was
16 introduced by the so-called “stacked-planar” model [6,10], where we assumed that the atoms are
17 randomly packed in a layer, which is then equidistantly stacked along the orthogonal direction (Figure
18 2 b)). The obtained arrangement of atoms thus presents a layered structure, which is amorphous in a
19 plane, and periodic in the third direction in accordance with the basic structural properties of the 2D
20 quasicrystals. The basic difference between the spherically isotropic Czjzek model and the “stacked-
21 planar” model is in the distribution of the parameters θ in ϕ , where in the last model the anisotropy is
22 clearly introduced. Besides, the difference between the two models appears also for distribution of the
23 parameters v_Q and η . In the spherically isotropic Czjzek model, the probability of finding an EFG with
24 $\eta = 0$ is zero, whereas it is nonzero in the “stacked-planar” model as seen from Figure 3 a). The
25 distributions $Q(v_Q)$ of the two models are qualitatively similar (Figure 3 b)). The peaks of the
26 “stacked-planar” model are somewhat narrower and a more pronounced gap around the zero value is
27 seen compared to the spherically isotropic Czjzek model.
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31 We were surprised that a model distribution of EFGs, which basically holds for 3D or 2D
32 amorphous solids, explained so well also the NMR spectra of the long-range ordered icosahedral and
33 decagonal quasicrystals, respectively. For comparison between the experiment and theory in the case
34 of the rotation about the twofold rotation of the decagonal Al-Ni-Co quasicrystal see Ref. [6]. One
35 possible explanation for such agreement may be the following. Namely, real quasicrystals exhibit a
36 large amount of chemical and sometimes also structural disorder, which is supported by X-ray
37 measurements [10]. On the other hand, a further insight can be obtained by replacing 2D amorphous
38 layer in the “stacked-planar” model with the 2D Penrose tiling. It turns out that it is crucial what type
39 of charges are placed at the centers of hard spheres or at vertexes of 2D Penrose tiling, respectively,
40 when calculating the distribution of EFGs.
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49 [Insert Figure 3 about here.]
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52 If random charges $\pm q$ are used, corresponding to the complete chemical disorder, than no
53 anisotropy can be observed within the layer perpendicular to the periodic (tenfold) axis even when
54 replacing 2D amorphous layer with the 2D Penrose tiling. This is best seen by calculating a histogram
55 (see Figure 3 c)) displaying the distribution of a polar angle φ , which defines the orientation of the
56 largest eigenvalue of the EFG tensor with respect to the crystal coordinate system where the z -axis
57 coincides with the tenfold axis. Consequently, by applying such model it is not possible to account for
58 the weak angular dependence in the NMR spectrum for rotation about the tenfold axis (Figure 1 d)).
59 On the other hand, if only positive charges $+q$ are used, which mimics a perfect chemical order, only
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4 some orientations of the EFG tensors are pronounced (see Figure 3 d)), obeying the tenfold symmetry
5 and explaining the observed angular dependence of the NMR spectrum about the tenfold axis.
6

7 **4 Acknowledgements**

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11 understanding of our results in combination with X-ray measurements done by his collaborator
12 Thomas Weber. We also thank Michael Feuerbacher from Jülich for provision of the decagonal
13 $\text{Al}_{72.6}\text{Ni}_{10.5}\text{Co}_{16.9}$ quasicrystal.
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Figure 1

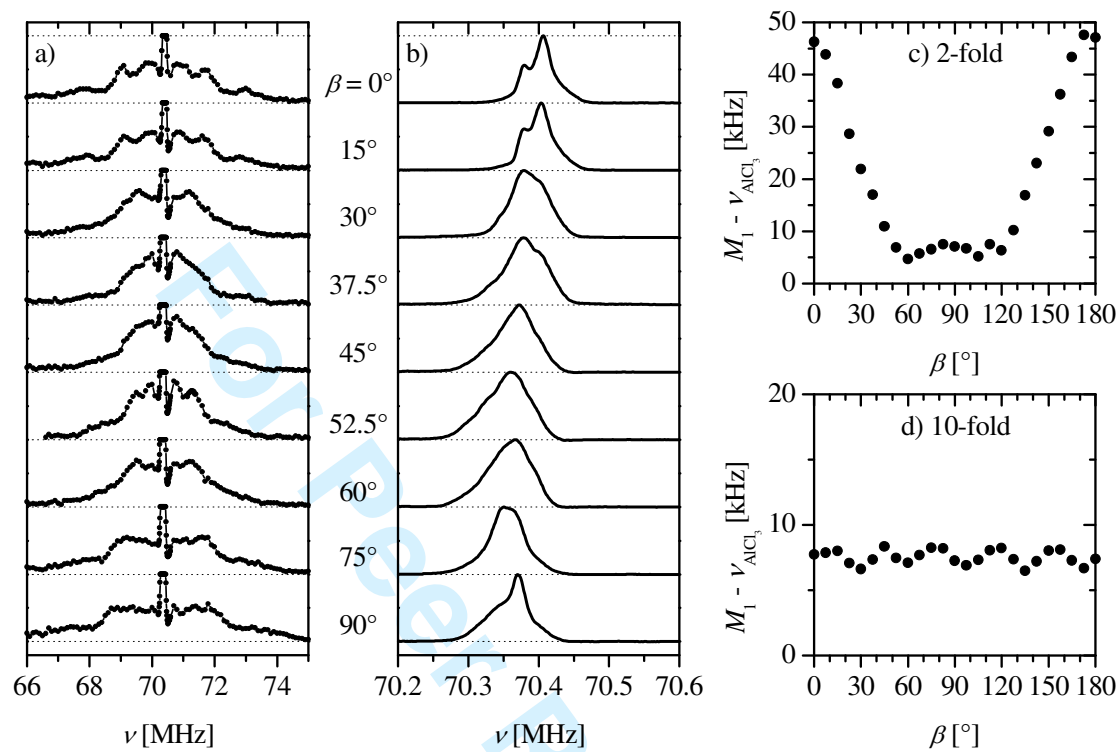
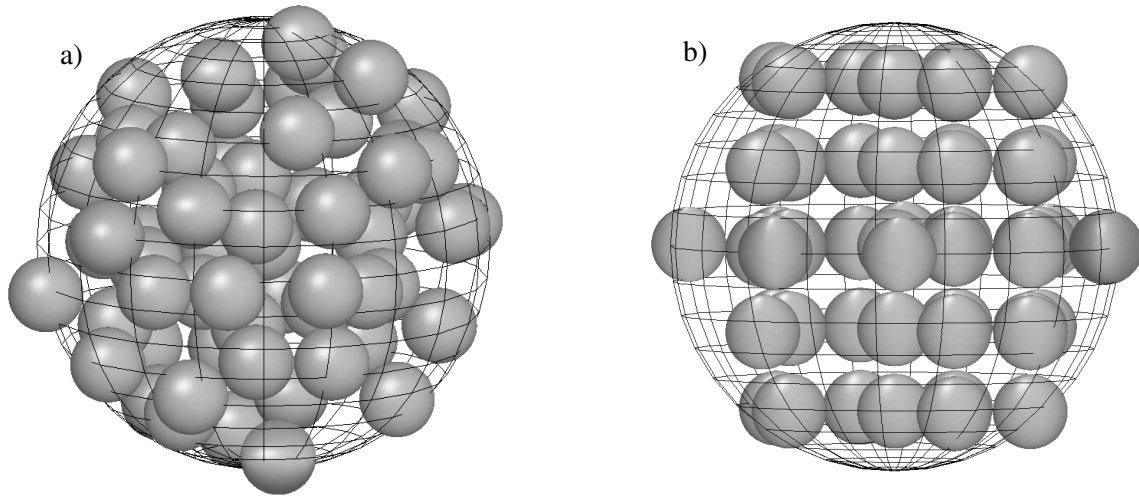


Figure 2



er Review Only

Figure 3

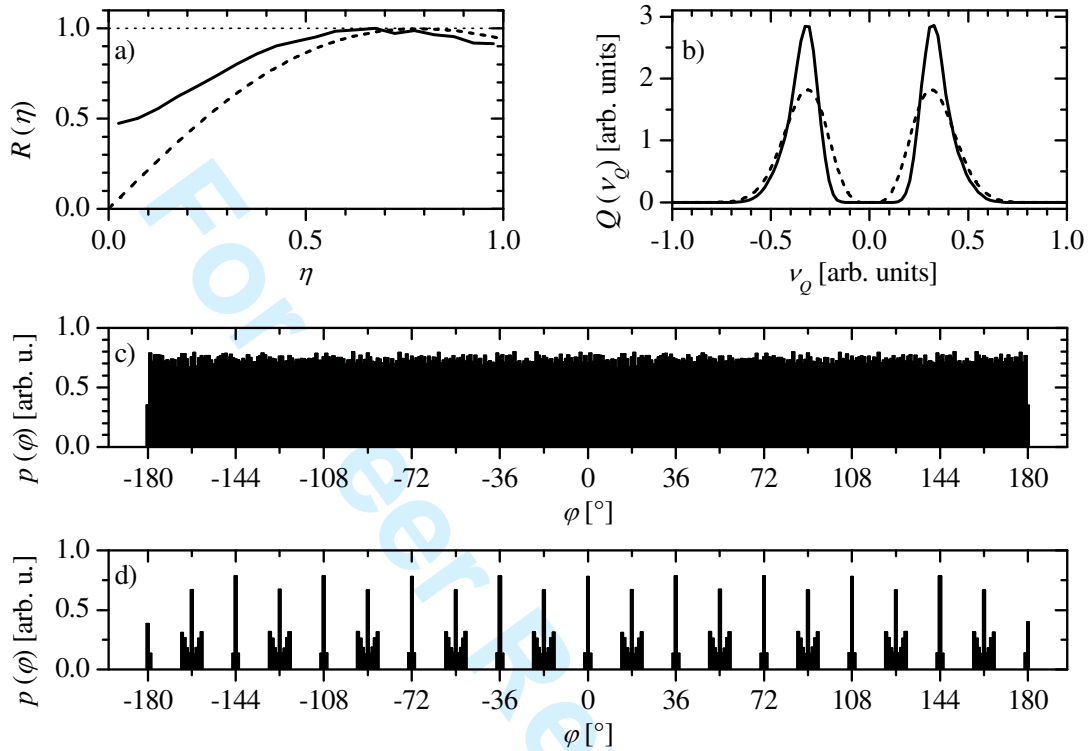


Figure captions

Figure 1. a) Orientation-dependent ^{27}Al NMR spectra at 80 K of the decagonal $\text{Al}_{72.6}\text{Ni}_{10.5}\text{Co}_{16.9}$ quasicrystal for rotation about the twofold axis on an expanded vertical scale, so that the satellite intensity is clearly visible, whereas the central line is clipped on this scale. In b) the central lines are separately displayed. Angular dependence of the center of gravity (the first moment M_1) relative to AlCl_3 of the ^{27}Al central lines for c) rotation about the twofold axis and d) rotation about the tenfold axis. Here β is the angle between the tenfold axis and the direction of the external magnetic field B_0 , except in the last figure, where it is simply an angle describing the rotation about the tenfold axis.

Figure 2. a) Atomic structure used to simulate the amorphous solid in the spirit of the work presented by Czjzek *et al.* Ions with random charge $\pm q$ are represented as hard spheres with radius R_{ion} . For each randomly obtained configuration of atoms, the EFG is calculated in the center of a sphere including only the charges within the radius $6R_{ion}$. b) Analogous atomic structure used in the simple model for the calculation of the NMR spectrum of 2D QCs. The layers are periodically stacked along one direction, whereas the atomic order within the layers is amorphous.

Figure 3. Marginal distributions a) $R(\eta)$ and b) $Q(v_Q)$ (solid lines) obtained from the “stacked-planar” model and used to calculate the theoretical NMR spectra shown in Ref. [6]. The corresponding theoretical distributions of the spherically isotropic Czjzek model are shown for comparison as dashed lines. In c) and d) the distribution of the polar angle φ (for definition see text) in the “stacked-planar” model with 2D Penrose tiling is shown. In c) random $\pm q$ charges are used for calculation of EFGs while in d) all charges have the same value $+q$. Note that at -180° and $+180^\circ$ only half of the joint intensity is visible.

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