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LETTER TO THE EDITOR

ORIENTATION-DEPENDENT NMR SPECTRA OF A SINGLE-GRAIN ICOSAHEDRAL Al-Pd-Mn QUASICRYSTAL

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Dedicated to Professor Boran Leontić on the occasion of his 70$^{\text{th}}$ birthday

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Orientation-dependent ^{27}Al quadrupole-perturbed NMR spectra of a single-grain $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal are reported. The dependence on orientation is a consequence of a spatially anisotropic distribution of orientations of the electric field gradient tensor at the inequivalent lattice sites. The results demonstrate that the NMR spectra of quasicrystalline single-grain samples of a macroscopic symmetry as high as icosahedral are orientation-dependent and differ from the orientation-independent spectra of powder samples, in contrast to previous reports.

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Quasicrystals [1] (QC) are solid materials exhibiting a new type of a perfect long-range order (LRO) without translational periodicity. Their symmetries (icosahedral, dodecagonal, decagonal, octagonal and pentagonal) involve "forbidden" symmetry elements such as 5-fold rotation axes that are incompatible with the periodicity of a Bravais lattice. A consequence of nonperiodicity is that phonons and electrons cannot propagate easily through the lattice, so that QC's, although alloys of metallic elements, exhibit transport phenomena that resemble more insulating than metallic solids. Quasiperiodic LRO can be constructed by using a certain non-random generation procedure to create atomic positions in space. The quasiperiodic lattice is built up by adding the atoms in space around some point of origin according to a well-defined mathematical prescription on the distances and angles between neighbouring atoms. The resulting structure is long-range ordered in a sense that any atomic position in the lattice is exactly predicted by the set of generic rules. Thus, there exists no randomness in the quasiperiodic structure, and a consequence of the LRO are sharp Bragg peaks in the X-ray diffraction pattern. There exist many non-random procedures to fill an empty space with atoms densely, but only a few of them result in structures exhibiting forbidden symmetries, named as quasiperiodic, that have no repetition distance in space. The simplest examples are the one-dimensional (1D) Fibonacci chain and the 2D pentagonal Penrose lattice.

One of the interesting open questions in the context of QC structures remains the local site symmetry of the lattice sites and the possible existence of short range order (SRO) on the atomic scale. The lack of translational periodicity implies that any atom in the quasiperiodic lattice is in principle located in a different chemical environment, characterized by a different arrangement of neighbouring atoms. If this were not so, one could define a block of atoms (a unit cell) that would repeat periodically over the lattice and would represent a translationally periodic rather than quasiperiodic structure. The definition of a periodic crystal is that only a finite number of different chemical environments exists that are repeated periodically over the lattice. Since the quasicrystalline order never repeats in space, every atom has its own unique arrangement of neighbours, resulting in an infinite number of inequivalent lattice sites. This conclusion is obvious when considering the atoms inside a large enough volume. On a small spatial scale, however, by considering the close neighbours only, the number of different chemical environments cannot be infinite. This is a consequence of the fact that the quasiperiodic lattice is built by obeying a small number of well-defined rules on how to add the atoms in the structure. On a small scale, only a finite number (possibly small) of different chemical environments can exist, and their number increases with the volume inside which the environment is defined. A kind of SRO should thus exist in QC's.

The existence of an infinite number of different chemical environments in QC structures on a large scale implies similarity to structures with an amorphous or glassy-type disorders. Amorphous structures are also nonperiodic, but in contrast to QC's, they are characterized by the absence of both LRO and SRO. Glassy structures (e.g. orientational-, spin-, proton- and quadrupolar glasses) are nonperiodic as well and exhibit no LRO, but on a small scale they look ordered as in perfect crystals and thus exhibit SRO. In view of the above similarity as well as differences, an interesting question arises whether the physical properties of QC's can be spectroscopically distinguished from those of amorphous and glassy structures.

In this paper we show that quasiperiodic order, though creating in principle an infinite number of chemically different local environments, produces an NMR spectrum that depends on the orientation of the single-domain QC sample with respect to the external magnetic field. The angle-dependent ^{27}Al quadrupole-perturbed NMR spectrum was observed in icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ which demonstrates the existence of inequivalent lattice sites that are realized with a higher probability than the others. The observation of angle-dependent NMR spectra in QC's makes it possible to discriminate between monodomain samples of quasiperiodic and amorphous order and between a monodomain and powder QC samples.

It is well known that the ^{27}Al ($I = 5/2$) NMR spectrum of icosahedral QC's, such as the Al-Cu-Fe(Ru) [2] and Al-Pd-Mn(Re) [3–7] families, is strongly inhomogeneously broadened. The spectrum shows a typical structure of a broad line, representing first-order quadrupole-perturbed satellite transitions, and a narrow central line (quadrupole-perturbed in second order) in the middle. The origin of the inhomogeneous broadening is the large multiplicity of inequivalent ^{27}Al sites. It was demonstrated that the shape and width of the ^{27}Al NMR spectrum are determined predominantly by the electric quadrupole interaction between the ^{27}Al nuclei and the electric field gradient (EFG), produced by the charges of the neighbouring ions and electrons [2]. Magnetic hyperfine interaction between the nuclei and the electronic magnetic fields is much weaker and can be to a good approximation neglected when static NMR parameters are considered. The origin of the EFG is twofold. A part of it comes from the external ionic charges and is enhanced by the Sternheimer antishielding effect due to the ionic electric field polarization of the core electrons, whereas the second part originates from the conduction electrons. The largest component V_{zz} of the EFG tensor in the principal axis system (PAS) can be written as

$$V_{zz}^{\rm tot} = V_{zz}^{\rm ion}(1 - \gamma_\infty) + V_{zz}^{\rm el}\,, \tag{1}$$

where $(1-\gamma_\infty)$ is the Sternheimer antishielding factor. The relative sizes of the ionic and conduction-electron contributions in QC's are not known, but a comparison to simple metals indicates that the electronic contribution in majority of metals is about three times larger than the lattice contribution and of opposite sign [2]. The exact calculation of the total EFG in QC's (as well as in ordinary metals) is difficult as it requires the knowledge of both ionic positions and their valence, and the wave functions of the conduction electrons. It is, however, reasonable to assume that the local symmetry of the total EFG tensor at a particular Al site is determined by the distribution of ionic charges around that site, so that the asymmetry parameters $\eta = (V_{xx} - V_{yy})/V_{zz}$of the ionic and electronic contributions are the same. We also adopt the assumption [2] that the magnitude of the electronic contribution does not vary appreciably over the Al sites, whereas the magnitude of the lattice contribution varies through the distribution of local environments. The above approximations thus attribute the average magnitude of the total EFG to the conduction-electron contribution, whereas the distributions of magnitudes and PAS orientations are attributed to the lattice contribution. Within this model, the electric-quadrupole-induced inhomogeneous broadening of the spectrum originates from the multiplicity of local chemical environments.

Since NMR is a local spectroscopic technique, the quadrupole-perturbed NMR frequency of a given Al nucleus depends on the magnitude of the EFG tensor (on the values of V_{zz} and η in the PAS) and the orientation of the PAS at that site. The orientation is expressed in terms of Euler angles θ and ϕ between the PAS and $\bar{B}_0$. An isotropic distribution of PAS over θ and ϕ in a monodomain sample results in an orientation-independent spectrum, which is the same as that of a powder specimen. For a powder of a regular, translationally periodic crystal, where all nuclear sites experience the same EFG, the spectrum exhibits a typical shape exhibiting singularities that depend on the asymmetry parameter η. Such a crystalline powder spectrum for a nucleus of a spin $I = 5/2$ is shown in Fig. 1c. In QC's, there exists a broad distribution of magnitudes of the EFG tensor, as demonstrated by the strongly inhomogeneously broadened ^{27}Al NQR spectra of $Al_{70}Cu_{15}Ru_{15}$ and $Al_{65}Cu_{23}Fe_{12}$ [2]. Zero-field NQR spectra are insensitive to the orientation of the PAS but depend on the magnitude of the EFG tensor only. In a monodomain QC sample, the distribution of EFG magnitudes smears out the possible fine structure (singularities) in the quadrupole-perturbed NMR spectrum, but does not introduce angular dependence. The orientation-dependence comes solely from the fact that the distribution of PAS over the intervals $0 \leq \theta \leq \pi$ and $0 \leq \phi \leq 2\pi$ is not isotropic, but some $\theta,\ \phi$ values are preferred.

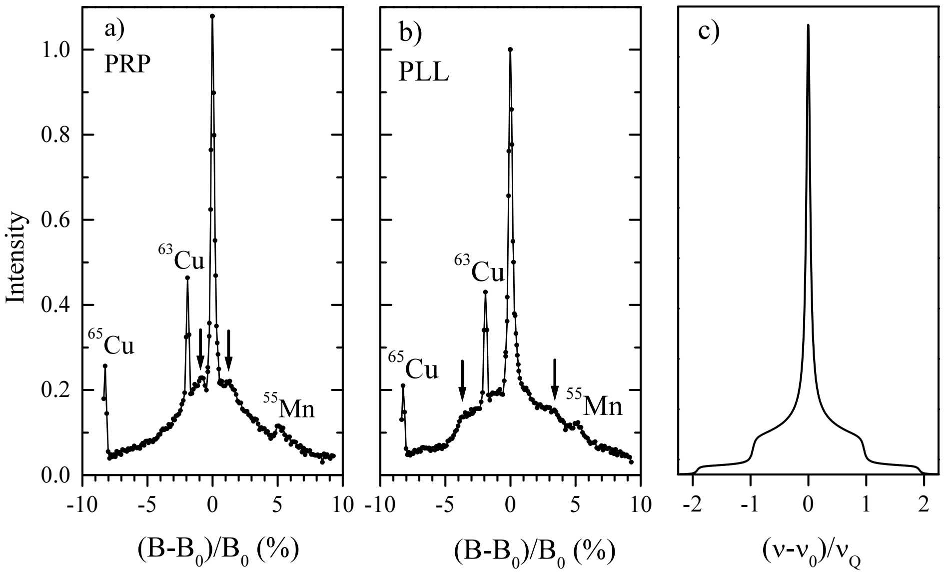

Fig. 1: Orientation-dependent ^{27}Al *field-swept NMR spectra of a single-grain icosahedral* $Al_{72.4}Pd_{20.5}Mn_{7.1}$ *quasicrystal at room temperature* ($\nu_0(^{27}\mathrm{Al} = 26.134\ \mathrm{MHz}, B_0 = 2.35\ \mathrm{T})$. *(a) 5-axis perpendicular to* $\bar{B}_0$ *(PRP orientation), with the arrows indicating the two peaks at ±1% in the satellite part of the* ^{27}Al *spectrum. (b) 5-axis parallel to* $\bar{B}_0$ *(PLL orientation), with the arrows indicating the two shoulders at ±4% in the satellite* ^{27}Al *spectrum. (c)* $I = 5/2$ *powder spectrum of a regular, translationally periodic crystal (all lattice sites having the same EFG) for* $\eta = 1$.

The orientation dependence of the ^{27}Al NMR spectrum was measured at room temperature in an icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ monodomain crystal, grown by the Czochralsky technique and further annealed at 800 °C. The same specimen was used before in an NMR study of the atomic self-diffusion [3]. The spectra were obtained by a magnetic field-sweep technique where the spin-echo intensity was recorded as a function of the field strength. The irradiation frequency was set to $\nu_0(^{27}\mathrm{Al}) = 26.134$ MHz (corresponding to the center absorption field $B_0 = 2.35$ T), and the monocrystal was oriented in the magnetic field with the 5-axis either parallel or perpendicular to $\bar{B}_0$ (in the following referred to as PLL and PRP orientations). The spectra are displayed in Figs. 1a and b. The high-intensity narrow line in the middle of the spectrum represents the ^{27}Al central $(1/2 \leftrightarrow -1/2)$ transition, whereas the broad line corresponds to the $(\pm 5/2 \leftrightarrow \pm 3/2)$ and $(\pm 3/2 \leftrightarrow \pm 1/2)$ sattelite transitions. Three other resonances are observed to overlap with the ^{27}Al spectrum. The ^{55}Mn line is located at +5.3% field relative to B_0, whereas the ^{63}Cu and ^{65}Cu lines are located at -1.7% and -9%, respectively. The ^{55}Mn line originates from the $Al_{72.4}Pd_{20.5}Mn_{7.1}$ sample, whereas the two copper lines come from the probehead coil. There is a quite pronounced difference between the PLL and PRP ^{27}Al spectra. The central lines of both spectra have the same intensity (integral), but the central line of the PRP spectrum is narrower and higher than that of the PLL (Fig. 2a). The difference is even more evident on the satellite lines. The PRP spectrum shows a narrower and higher satellite line that exhibit two symmetric peaks close to the central line (at ±1% of B_0). The PLL satellite spectrum, on

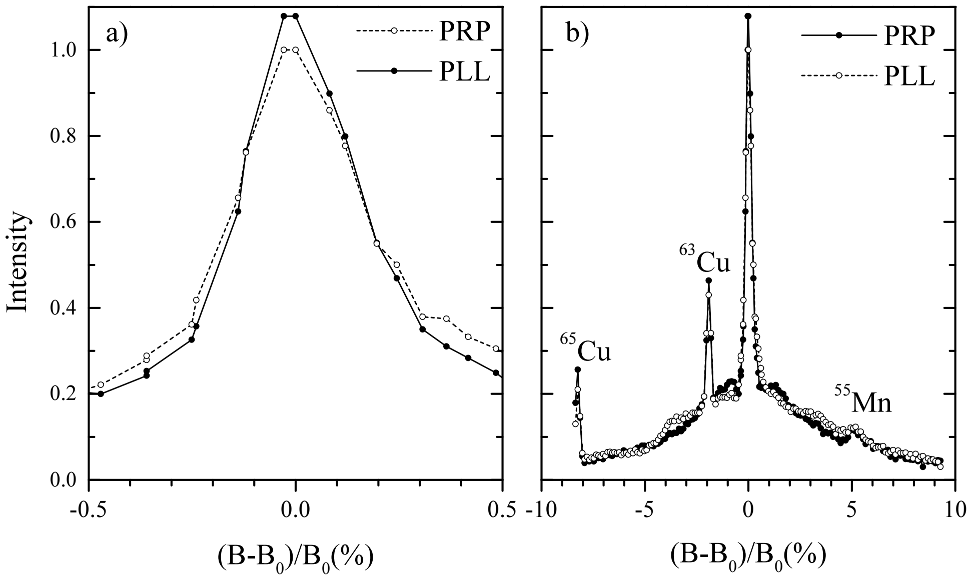

Fig. 2: (a) Central lines of the PRP and PLL spectra from Fig. 1 shown on an expanded scale. (b) PRP and PLL spectra superimposed on each other. The difference of the two spectra, due to the orientation-dependence, is clearly visible.

the other hand, is broader and lower in amplitude and does not exhibit resolved peaks. Instead, two well pronounced shoulders are observed at $\pm 4\%$ (the shoulder at $+4\%$ is less visible due to the overlap with the ^{55}Mn line). The PLL line shows some similarity to the $I = 5/2$ crystalline powder spectrum for $\eta = 1$, exhibiting similar shoulders (Fig. 1c), whereas the two-peak structure of the PRP line cannot be reproduced within the crystalline powder model. The angular dependence of the spectra is clearly demonstrated in Fig. 2b where the PRP and PLL spectra are superimposed on each other. The differences are far above the experimental uncertainty.

In view of an infinite number of sites with different chemical environments in the quasiperiodic lattices, the orientation dependence of tensorial physical properties, like the electric quadrupole interaction in an NMR lineshape experiment, does not appear obvious. The angular dependence of the spectra originates from the fact that some types of the atomic arrangements are preferred. The EFG at a given lattice site is a short-range physical quantity. In a point-charge model the ionic gradient is given by $\sum_i e_i/r_i^3$, where r_i is the distance to the external charge e_i. Due to the $1/r^3$ dependence, only the charges in the few nearest coordination shells contribute to the EFG that is thus sensitive to the near environment, and consequently to SRO only. In QC's, the number of different close environments cannot be very large and the restriction comes from the mathematical construction rules. This can be simply illustrated in 1D for a Fibonacci chain, but similar arguments apply also to 2D and 3D QC structures. It is well known that a Fibonacci quasicrystal is constructed by placing the atoms on a straight line in a way that the distance between two neighors is either long (L) or short (S). The structure is built in iterative steps starting from L, where in each step the substitutions L $\rightarrow$ LS and S $\rightarrow$ L are made. If the ratio L/S is an irrational number, this sequence has no repetition distance in space, but still shows a perfect LRO. The substitution rules imply that in the final structure every S has always two L nearest neighbours, forming a string LSL, whereas there are three possible nearest-neighbour combinations with L in the middle; SLS, LLS and SLL. When the next-nearest neighbour shell is taken into account, one notes that only two neighbouring L's are possible in a sequence (the LL string). This implies that the number of next-nearest neighbour strings with L in the middle still remains three only (LSLSL, SLLSL, LSLLS) and is not increased with respect to the nearest-neighbour case. In the case that the substitution rules would not be respected, but the structure would be built in a random way with equal probabilities of having L or S for the nearest neighbour on each side, the number of next-nearest neighbour strings would increase to sixteen already. Such a random generation procedure would result in an amorphous structure with neither LRO nor SRO. One can continue to add the next-next-nearest neighbours and so on in the calculation of the ionic EFG and count the number of possible atomic environments around a given central atom. It is easy to see that for the Fibonacci chain, this number will stay small, whereas for a random structure, it will grow enormously. Due to the $1/r^3$ short-range contribution of the charges to the EFG, adding more and more remote neighbours actually will not alter the EFG any more. The short-range nature of the interaction also indicates that the effect of angular dependence should be very similar in monodomain quasicrystals with perfect quasiperiodic order and in their large-scale crystalline approximants. The relatively small number of near-neighbour local environment on a small scale in QC's (though infinitely many on a large scale), together with the short range nature of the electric quadrupole interaction, is responsible for the observed orientation-dependence of the ^{27}Al NMR spectrum in $Al_{72.4}Pd_{20.5}Mn_{7.1}$. The comparison of the experimental ^{27}Al spectra with the theoretical spectra of a crystalline powder, however, shows that the differences, though clearly visible, are not large and can be detected only in a high-precision measurement. This demonstrates that the multiplicity of the inequivalent Al sites in the icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ is indeed very large and the distribution of the EFG tensor PAS orientations is not far from isotropic.

The above study reports the first observation of the orientation-dependent NMR spectra in quasicrystals. The results contradict the common belief that the NMR spectra of monodomain QC samples are orientation-independent and equal that of a QC powder specimen. The observed angular dependence results from the distribution of the EFG tensor orientations that is non-uniform in space. This confirms the existence of SRO in quasicrystals that exists in addition to the nonperiodic LRO.

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SPEKTRI NMR JEDNOG ZRNA IKOSAEDARSKOG Al-Pd-Mn KVAZIKRISTALA OVISNI O SMJERU

Ustanovili smo ovisnost kvadrupolno-smetanih spektara NMR ^{27}Al u jednom zrnu ikosaedarskog kvazikristala $Al_{72.4}Pd_{20.5}Mn_{7.1}$ o smjeru. Ta je ovisnost posljedica prostorno neizotropne raspodjele tenzora gradijenta električnog polja na različitim položajima u rešetci. Ishodi mjerenja pokazuju da spektri NMR kvazikristalnih jednozrnih uzoraka tako visoke simetrije kao što je ikosaedarska ovise o smjeru i razlikuju se od smjerno-neovisnih spektara praškastih uzoraka, što je suprotno ranijim izvješćima.