Anomalous NMR response of quasicrystalline icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ at low temperatures

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We report the observation of an anomalous ^{27}Al-NMR response of a single grain $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal at low temperatures. In an external magnetic field of 6 T and upon decreasing temperature, we observe a sharp 100% increase of the resonance linewidth at 2.5 K. No further changes of the linewidth are observed down to 0.05 K. The linewidth enhancement is accompanied by a small but distinct increase of the spin-lattice relaxation rate T_1^{-1}. These anomalies are absent in external fields of 2.5 T and below. Our observations indicate unusual variations in the stability of isolated magnetic moments in a quasiperiodic metallic environment.

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Various physical properties of icosahedral quasicrystals of Al-Pd-Mn alloys have been studied in recent years. Especially intriguing are their magnetic properties.[1–3] For example, from data of the magnetic susceptibility and the specific heat, as well as from the results of calculations of the electronic structure,[1,4,5] it has been inferred that in these materials only a small fraction, of the order of 1%, of Mn ions carry a magnetic moment. The coexistence of magnetic and nonmagnetic Mn sites in Al-rich quasicrystals has also been discussed for Al-Pd-Mn quasicrystals with slightly varying chemical composition.[6–8] The formation or the absence of ionic magnetic moments at the Mn sites in Al-Pd-Mn quasicrystals has first been attributed to differences in the local chemical environment of the Mn ions. In particular it was claimed[4] that a weak Al-p-Mn-d hybridization leads to the formation of well localized and rather large Mn moments. More recently, however, it has been suggested[5] that the local environment of the Mn ions alone cannot explain why only few Mn ions carry a magnetic moment and that also Mn-Mn interactions over large distances ought to be taken into account.

Previous ^{27}Al NMR experiments[3] on a single grain quasicrystal with a composition of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ have shown that the small number of magnetic Mn ions decreases even further with decreasing temperature below approximately 20 K. This unusual behavior in this temperature range was revealed by a reduction of the NMR linewidth with decreasing temperatures, as well as by indicative features of the temperature dependence of the magnetic susceptibility $\chi(T)$. In this work we present experimental evidence for additional anomalies in the temperature dependencies of the NMR spectra and the spin-lattice relaxation rate T_1^{-1} of an icosahedral $Al_{72.4}Pd_{20.5}Mn_{7.1}$ quasicrystal. In external magnetic fields of the order of 6 T and with decreasing temperature we observe drastic changes in the temperature dependencies of both the ^{27}Al- and the ^{55}Mn-NMR linewidth at $T_b = 2.5$ K, accompanied by a distinct variation in the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}(T)$. None of these anomalies is observed in fields of the order of 2.5 T or smaller.

The investigated sample was a single-grain piece of quasicrystalline material with a nominal composition of $Al_{72.4}Pd_{20.5}Mn_{7.1}$, grown by the Czochralski technique and annealed at 850 °C. Its chemical and structural quality has been discussed in Ref. 9. The same sample, previously used to perform measurements of ^{27}Al-NMR spectra at higher temperatures,[3] has also been characterized by measurements of the magnetic susceptibility and the electrical conductivity between 1.5 and 300 K.[3] In all our NMR experiments, standard spin-echo techniques have been employed. The NMR spectrum was measured using spin-echo sequences of the form $\pi/2 - \tau - \pi$ with the length of the π pulse of the order of 10 μs and τ between 40 and 80 μs.

In Fig. 1(a)–(c) we present the central part of the ^{27}Al-NMR spectra of our sample, measured at the Larmor frequency of 71.33 MHz, at three different temperatures. The well defined peaks in the spectra represent the central Zeeman transition $(1/2 \leftrightarrow -1/2)$ of the Al nuclei. Unlike the central line, which is quadrupolar perturbed in second order, the wings of the spectrum, i.e., the $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ satellite transitions, are perturbed in first order. The lack of translational periodicity implies that the satellite intensity is distributed over a broad range of resonant fields.[10] The shape and full width of the wings do not reveal T-induced changes, as shown in Fig. 2 for $T = 3$ and 20 K. Thus the anomalous temperature dependence of the NMR linewidth below 20 K shown in Fig. 3 is most probably of magnetic and not of electric quadrupolar origin. Hence the following discussion considers the central transition only.

Two sharp features can clearly be distinguished in the temperature dependence of the ^{27}Al-NMR linewidth Δ [full width at half maximum (FWHM)] measured at 67 MHz (see Fig. 3). These are, a discontinuity in Δ and a break in its slope at $T_b = 2.5$ K and $T_a \approx 15$ K, respectively. Above T_b there are only very modest field-induced changes in Δ which, at first sight, may seem surprising but, in fact, it is expected in our case.[11] As may also be seen in the same figure, Δ decreases substantially with decreasing temperature between T_a and T_b. This loss of linewidth, already reported in Ref. 3, is recovered almost discontinuously at T_b and

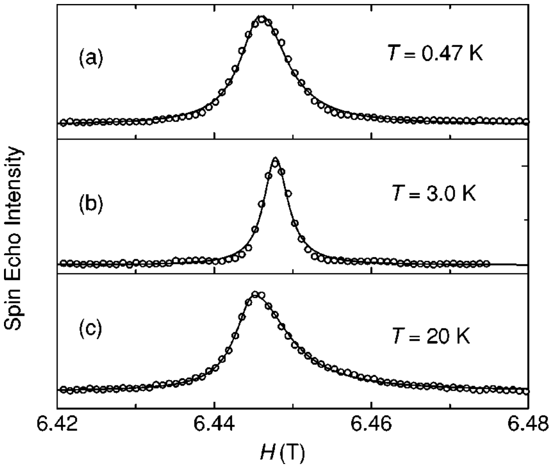

FIG. 1. Central part of the ^{27}Al-NMR spectra of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal measured at 71.33 MHz and three temperatures. The solid lines represent the best fits to the data using a Lorentzian-type function with a degree of asymmetry built into it.

$\Delta(T)$ is approximately constant below that temperature. This particular behavior is observed at Larmor frequencies of 67.00 and 45.75 MHz, but is absent in much lower magnetic fields. This is emphasized in Fig. 3, where also $\Delta(T)$ of the central ^{27}Al Zeeman ransition for spectra measured at 26.00 MHz, corresponding to an applied magnetic field 2.5 T, is displayed. While $\Delta(T)$ is approximately the same for both cases between T_a and T_b, no discontinuous enhancement of Δ is manifested in the data set measured at 26 MHz.

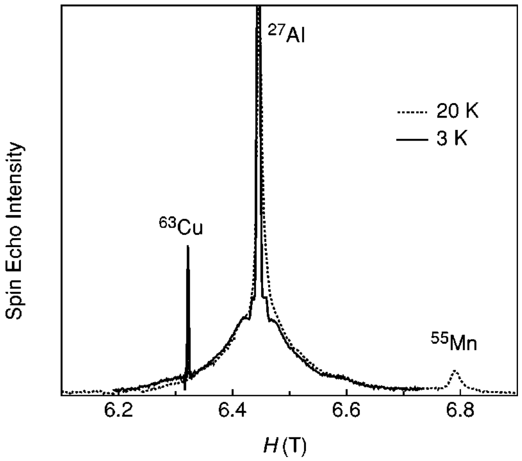

FIG. 2. Full NMR spectra $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal measured at 3 and 20 K. The ^{63}Cu signal is from the NMR detection coil.

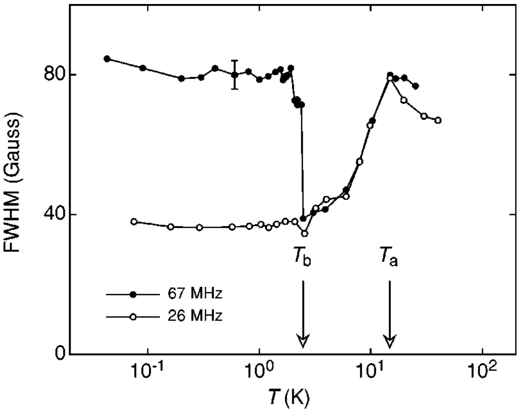

FIG. 3. ^{27}Al-NMR linewidth Δ as a function of temperature for data measured at 26.00 and 67.00 MHz. Sharp features are observed in $\Delta(T)$ for the data measured at 67 MHz at $T_a = 15$ K and $T_b = 2.5$ K. The solid lines are guides to the eye.

In Fig. 4 we show three examples of ^{55}Mn-NMR spectra, recorded at a fixed frequency of 71.33 MHz and at temperatures of 0.48, 3.0, and 20 K. The central transition ($1/2 \leftrightarrow -1/2$) of the ^{55}Mn nuclei is centered at approximately 6.79 T. The ^{55}Mn nuclei carry a spin of $I = 5/2$ and exhibit a relatively large electric-quadrupole moment. Also here, the quadrupolar wings are expected to be widely spread out and indeed, they cannot be resolved in our experiments. Considering the small line shift, of the order of -0.3%, as well as the moderate linewidth monitored in the ^{55}Mn-NMR central transition, we conclude that the observed Mn-NMR signal originates from Mn nuclei of nonmagnetic ions. Because of the expected generation of large hyperfine fields the resonance of the nuclei of magnetic Mn ions is assumed to be outside our observation range. By comparing the integrated intensities of the recorded central lines for ^{27}Al and ^{55}Mn nuclei, and taking into account the differences in the intrinsic NMR intensities for ^{27}Al and ^{55}Mn, we conclude that at most a few percent of the Mn ions carry a magnetic moment.

As in the case of the ^{27}Al NMR spectra, Fig. 4 reveals that the linewidth of the ^{55}Mn central transition in the spectrum measured at 3.0 K is smaller than the corresponding linewidths at 0.48 and 20 K. Again, upon decreasing T, an abrupt increase of the FWHM Δ of the ^{55}Mn signal is observed at T_b in various fields of the order of 4 T or higher.

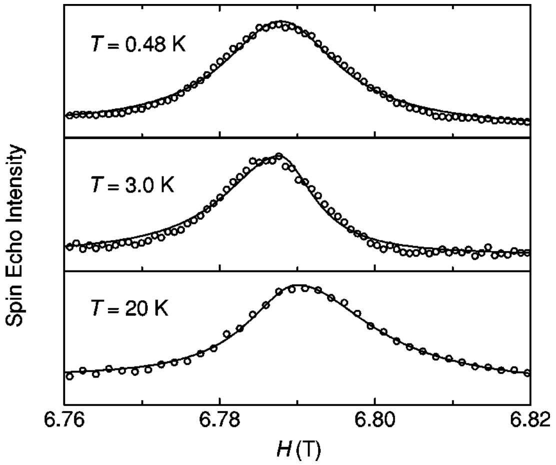

FIG. 4. Central transition of the ^{55}Mn-NMR spectra of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal measured at 71.33 MHz and three temperatures. The solid lines represent the best fits to the data using a Lorentzian-type function with some degree of asymmetry built into it.

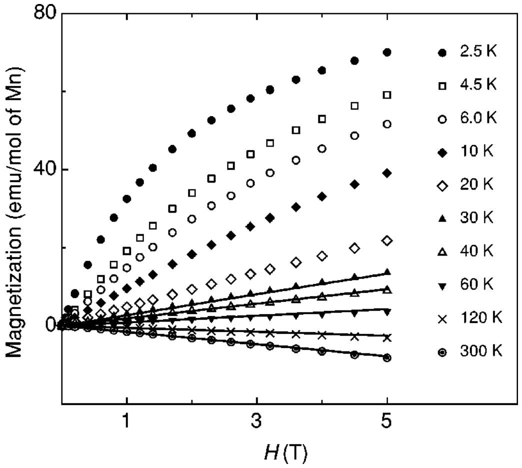

FIG. 5. Magnetization as a function of applied field of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ icosahedral quasicrystal measured at several temperatures. The solid lines represent the best fits to the high-temperature data as described in the text.

Various checks, with measurements performed using different conditions for the signal recording, indicate that this abrupt change of the linewidth, not explicitly shown here, is a rather robust feature for this quasicrystalline material and it is very unlikely that it is caused by extraneous artifacts of the measurements.

We emphasize that no sharp anomalies have been observed[3] in the temperature dependence of the magnetic susceptibility $\chi(T)$ of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ at temperatures above 2.5 K. From the data displayed in Fig. 5 one may also conclude that there are no sharp anomalies in the temperature and field dependencies of the dc magnetization $M(H,T)$ for $T > 2.5$ K and $0 < H < 5$ T. We assume that $M(H)$ consists of a temperature-independent part associated with the Larmor diamagnetism of the sample and a contribution due to magnetic moments $M_{loc}(H)$ localized at some Mn sites. The high-temperature, $T > 20$ K, data is well fitted (solid lines in Fig. 5) by taking $M_{loc}(H,T) \propto H/(T-\theta)$ with θ the paramagnetic Curie temperature. The results of these fits indicate that only a small fraction (of the order of 1%) of Mn ions carry magnetic moments and in our case $\theta = -23$ K. At lower temperatures the analysis of the data is more complicated. Here we simply point out that the sensitivity of the low-temperature magnetization to rather modest changes of H and T hints for a very small value for the low-temperature θ, of the order of 2 K or smaller. Again this is consistent with our results for $\chi(T)$ discussed in Ref. 3.

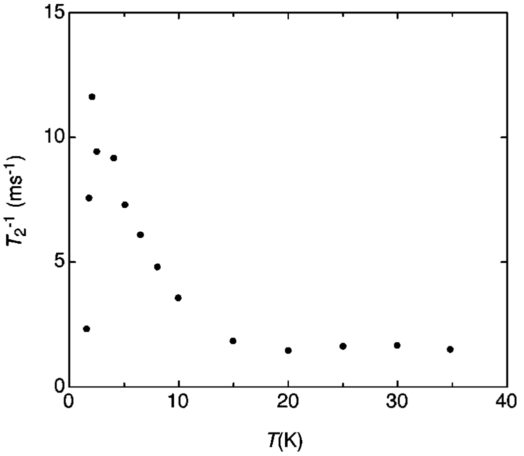

FIG. 6. Spin-spin relaxation rate T_2^{-1} as a function of temperature measured at the ^{27}Al-NMR central transition at 67 MHz.

We also investigated the NMR response of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ by measurements of the temperature dependence of the spin-spin relaxation rate T_2^{-1}. For this purpose the spin-echo lifetime $T_2^{\star}$ was first extracted from spin-echo decay curves, i.e., curves of the echo intensity as a function of the time delay τ between the two pulses of a $\pi/2 - \tau - \pi$ spin-echo sequence. The effective rate T_2^{-1} was then calculated via $T_2^{-1} = T_2^{\star -1} - T_1^{-1}$. The spin-lattice relaxation rate T_1^{-1} was measured separately and was found to be much smaller than $T_2^{\star -1}$ at all temperatures covered in our experiments. The results for $T_2^{-1}(T)$, evaluated for the ^{27}Al-NMR central transition at the Larmor frequency of 67.00 MHz, are displayed in Fig. 6. We note the gradual increase of T_2^{-1} with decreasing temperatures below T_a and, again near T_b, its rather abrupt reduction by more than a factor of 5. This overall behavior is to be compared with previous observations involving metals with atoms containing unfilled $3d$-electron shells, such as Mn, where one often finds, with decreasing T, a progressive increase of the NMR linewidth, an increase of $(T_1T)^{-1}$ and, if any, a reduction of T_2^{-1}. Both the reduction of the NMR linewidth and the increase of T_2^{-1} with decreasing T below T_a are thus unexpected, but they seem to be related to each other. Similarly, the sharp changes in the FWHM and in T_2^{-1}, observed at T_b, undoubtedly reflect a common cause.

In attempting a further characterization of the anomalous NMR response of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ at low temperatures, we have measured the temperature dependence of the NMR spin-lattice relaxation rate T_1^{-1} under various experimental conditions. To minimize spin-diffusion complications we have used very long combs of $\pi/2$ rf pulses to saturate the nuclear magnetization and the spin-echo intensity was recorded after a variable delay t. The T_1 values were obtained from the nuclear magnetization recovery curves. We have found no evidence for any appreciable quadrupolar relaxation contribution to T_1^{-1} in the $m(t)$ curves. As we will see below, this is further supported by the strong field dependence found for $T_1^{-1}(T)$. In Fig. 7 we display $(T_1T)^{-1}$ as a function of T, with T_1 measured at the central transition of the ^{27}Al nuclei, for two different applied magnetic fields of 1.147 and 6.054 T, corresponding to Larmor frequencies of 12.70 and 67.00 MHz, respectively.

Below T_b, $(T_1T)^{-1}$ gradually increases with decreasing temperatures. This is not unusual for quasicrystals[12,13] but remains an interesting unsolved problem. At this point our analysis is dedicated to data at temperatures $T > T_b$. For this purpose a small number of magnetic Mn ions has to be considered. The $\chi(T)$ data, exhibiting a Curie-Weiss-type feature above 20 K, reveals a small paramagnetic Curie temperature and an effective magnetic moment corresponding to

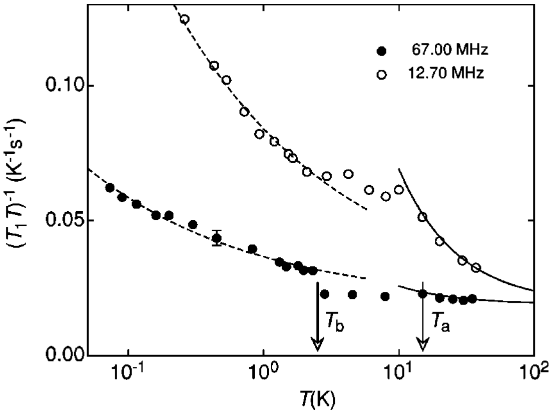

FIG. 7. $(T_1T)^{-1}(T)$ measured at the ^{27}Al-NMR central transition at 67.00 and 12.70 MHz. Above $T_a=15$ K, T_1^{-1} may be understood using a simple model which includes the contributions of the conduction electrons and isolated Mn magnetic moments (solid lines). The latter contribution, however, turns into a power law below $T_b=2.5$ K (broken lines).

a concentration $c\approx 1\%$ of magnetic Mn^{4+}, Mn^{3+} (both with quenched orbital moment), or Mn^{2+} ions. Consequently it seems appropriate to consider the remaining magnetic Mn ions as carrying isolated magnetic moments forming "paramagnetic impurities." For this case, neglecting spin diffusion complications,[14] the temperature and field dependencies of the nuclear relaxation rate $(T_1^{imp})^{-1}$, at temperatures where the random fluctuations of the impurity moments are not correlated, is given by[15,16]

$$\frac{1}{T_1^{imp}T}\propto c\cdot\frac{\langle S^z\rangle}{H}\cdot\frac{\tau}{1+(\omega\tau)^2}, \tag{1}$$

where τ is a time scale characterizing the spectrum of fluctuations of the impurity (correlation time) and $\langle S^z\rangle$ is the average z component of the impurity spins induced by H. In the spirit of this very simplified model we assume that $\langle S^z\rangle$ has a Curie-type temperature dependence.[17] The angular Larmor frequency $\omega\propto H$. Since our quasicrystalline material is metallic, an additional Korringa-type contribution to the spin-lattice relaxation rate via the conduction electrons $(T_1^{ce})^{-1}$ is expected.[18] In total,

$$(T_1T)^{-1}=(T_1^{ce}T)^{-1}+(T_1^{imp}T)^{-1}. \tag{2}$$

Indeed the experimental data above T_a are fairly well represented by invoking the above-mentioned interpretation. The solid lines in Fig. 7 are based on Eq. (2), both with the same value of $(T_1^{ce}T)^{-1}\approx 0.019$ K^{-1} s^{-1}, indicating that the relaxation via conduction electrons is field independent. This relaxation rate is very close to that reported in Ref. 19 for $Al_{75}Pd_{15}Re_{10}$ but by only a factor of 3 higher than the corresponding rate observed in nonmagnetic $Al_{70}Re_{8.6}Pd_{21.4}$.[12] This is rather surprising because the electrical conductivities $\sigma(T)$ of the Re alloys are, respectively, between one and two orders of magnitude lower than $\sigma(T)$ of our Al-Mn-Pd quasicrystal.[3,20] Thus this observation might indicate that the electrical transport in quasicrystals is not simply dictated by the number of itinerant charge carriers, but is dominated by scattering processes that are not well understood.

Because of the factor $(1+\omega^2\tau^2)^{-1}$ in Eq. (1), the magnitude of the second term in Eq. (2), due to the relaxation via impurity spins, is influenced by the strength of the external field. Our fits, considering the respective field values and assuming a temperature- and field-independent[21] correlation time τ in this temperature range, imply a very large value of $\tau=7\times 10^{-9}$ s^{-1}. This is orders of magnitude larger than those expected for dilute paramagnetic impurities in metals, such as Gd impurities in $LaAl_2$.[21] Since there is no obvious reason for an extremely weak coupling between the moments and the conduction electrons, the correlation time τ may be large because of the proximity of a magnetic phase transition at temperatures of the order of T_a, slowing down the moment fluctuations.

We note that the salient features in the T dependence of T_1^{-1} are definitely field dependent below T_a. The low-field data for $(T_1T)^{-1}$ exhibit a clear break in the slope $\partial(T_1T)^{-1}/\partial T$ at or very near T_a which may, in the most straightforward way, be interpreted as a change in the dynamics of the fluctuating impurities. Although there is no visible anomaly in $\chi(T)$ at T_a, measured in a field of 2 T, one observes a gradual slope change in $\chi(T)$ which is consistent with a gradual decrease of the number of magnetic Mn ions in this T range.

The high-field data differs in the sense that, if at all, the break in the slope of $(T_1T)^{-1}(T)$ at or very near T_a is barely visible, but instead a discontinuity in $(T_1T)^{-1}$ at T_b, concomitant with the discontinuous linewidth enhancement, is observed. Both in high and low fields, the linewidths are nearly temperature independent below T_b, but the relaxation rates T_1^{-1}, vary as $(T_1T)^{-1}=(T_1^{ce}T)^{-1}+C(H)\cdot T^{-0.35}$, represented by the broken lines in Fig. 7. Here $C(H)=0.018$ and 0.065 K$^{-0.65}$s^{-1} for the frequencies of 67 and 12.7 MHz, respectively. This assumes that the contribution of the conduction electrons to the spin-lattice relaxation rate is not altered very much at low temperatures, as suggested by the small changes of $\rho(T)$ observed in our sample below T_a.[3] In any case, the temperature and field dependencies of Δ and T_1^{-1} below T_a are very unusual. Although, our sample seems to be close to some kind of magnetic instability above T_a, our observations for the low-temperature regime $T\leqslant 15$ K cannot be reconciled with expectations, either for nonmagnetic hosts containing magnetic impurities, or for spin glasses or magnetically ordered systems. We emphasize that our data for $\Delta(T)$ [and also for $\chi(T)$, see Ref. 3] cannot easily be reconciled with a Kondo-type screening of the Mn magnetic moments, with $T_K\approx T_a$, because in the Kondo scenario the conduction-electron spin polarization, basically responsible for the hyperfine field distribution (i.e., responsible for Δ), varies with temperature as $1/(T+T_K)$,[22] leading to a monotonically increasing Δ with decreasing T, for all temperatures. This is not observed in our experimental results.

In conclusion, we report here the observation of unusual anomalies in the NMR response of an icosahedral AlPdMn quasicrystal. The low-temperature features of $Al_{72.4}Pd_{20.5}Mn_{7.1}$ observed in this work seem to indicate unusual variations in the stability of transition-metal (Mn) ionic moments in a nonperiodic metallic matrix at different temperatures. At present we have no convincing explanation for the observed phenomena (see also Ref. 3), but in view of the covered temperature regimes, they must be related to rather low characteristic energies.

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