

NMR Study of the Electronic Properties and Stability of Quasicrystals

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We have studied by NMR the electronic properties of the stable quasicrystalline phases $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$ and $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ and of two crystalline approximants, the bcc R phase $\text{Al}_{56}\text{Cu}_{12}\text{Li}_{32}$ and the rhombohedral $\text{Al}_{62.8}\text{Cu}_{26}\text{Fe}_{11.2}$ phase. Low values of the density of states at the Fermi level are observed in the crystalline as well as in the quasicrystalline phases. The existence of a pseudogap at the Fermi level is therefore not a consequence of the quasiperiodicity. These results renew the debate on the stability of quasicrystals.

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Much work has been devoted to the electronic properties of newly discovered stable quasicrystalline (hereafter qc) phases with icosahedral symmetry, such as Al-Cu-Li [1], Al-Cu-Fe [2,3], or Al-Cu-Ru [4], to decide whether or not the quasiperiodicity induces specific properties. A well-established common feature of all these qc phases is a high room-temperature resistivity which moreover increases as the temperature decreases. Such effects have been ascribed to localization effects, and the proximity of a metal-insulator transition has been evoked [3]. Low values of the electronic density of states at the Fermi level, $N(E_F)$, deduced from specific-heat measurements, have been reported. The reduction of $N(E_F)$ with respect to estimated free-electron values is about one-third in Al-Li-Cu [1] and Al-Cu-Fe [2,3]. It reaches one-tenth in Al-Cu-Ru [4]. This observation of a pseudogap at the Fermi level in qc materials is in agreement with theoretical predictions [5]. It has been suggested that this pseudogap could explain the thermodynamical stability of these qc phases, following a Hume-Rothery scheme [5-7].

The qc phases are found in a very narrow composition range of complex ternary phase diagrams. Several different crystalline phases usually exist with close compositions. Among these, the so-called approximant phases are especially interesting. The qc and approximant phases have very similar local order and exhibit closely related diffraction spectra. Within a theoretical point of view, the existence of approximants is quite natural [8]. Whereas the 3D quasiperiodic lattice is obtained from a 6D hypercubic lattice by a cut and projection along irrational directions of the 6D space, periodic approximants are obtained by projection along rational close directions. The period of such an approximant, of course, increases when the rational directions get closer to the irrational ones. Although the existence of approximants should be quite general, their identification in real phase diagrams is not always easy. The crystalline bcc phase $\text{Al}_{56}\text{Cu}_{12}\text{Li}_{32}$

(the so-called R phase) has been recognized early as an approximant of the icosahedral qc $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$ phase [9]. The existence of an approximant in the Al-Cu-Fe system was suggested by the observation of a microcrystalline structure with a rhombohedral symmetry in small dodecahedral particles extracted from an ingot [10]. However, this approximant phase has been only very recently prepared in appreciable quantity at CECM, Vitry, and its domain of existence (around $\text{Al}_{62.8}\text{Cu}_{26}\text{Fe}_{11.2}$) determined [11]. Its x-ray powder diffraction pattern coincides with the one calculated from the quasiperiodic pattern when approximating the golden number by the rational number $\frac{3}{2}$ [12].

The aim of the present paper is to carefully compare the electronic structure of the quasicrystals and of their crystalline approximants. Such a comparison must be done before discussing the stability of qc versus their electronic properties. Little is known about the electronic properties of the approximants apart from the resistivity of the R $\text{Al}_{56}\text{Cu}_{12}\text{Li}_{32}$ phase [11], which, in striking contrast with the qc phase, shows a normal metallic behavior with a decrease of the resistivity as the temperature decreases. The room-temperature resistivity of the R phase ($200 \mu\Omega \text{ cm}$) is 4 times smaller than that of the qc phase. In the following we will compare the density of states at the Fermi level, deduced from measurements of the nuclear relaxation time (T_1) of the Al nuclei in the icosahedral qc $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$, in the R phase $\text{Al}_{56}\text{Cu}_{12}\text{Li}_{32}$, in the icosahedral qc $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$, and in the rhombohedral $\text{Al}_{62.8}\text{Cu}_{26}\text{Fe}_{11.2}$ phase.

The Al-Li-Cu ingots have been prepared at Centre de Recherches, Pechiney (France) by slow cooling [9,13], and subsequently ground into powder. Neutron- [13] and x-ray-diffraction patterns of the NMR samples indicate that the qc phase contains a small amount of Al metal and of the hexagonal $T1$ Al_2CuLi phase, and that the R phase contains Al metal. The Al-Cu-Fe alloys were made at CECM, Vitry, by planar flow casting. The

$\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ flakes were then annealed at 800°C for 2 h. This procedure is known [12] to eliminate the small amount of β phase present in the as-quenched state, and to lead to a perfect icosahedral state. For this peculiar composition the perfect qc state has not been altered by any further annealing treatments at lower temperature and is therefore a possible ground state in the phase diagram [12]. The composition of the rhombohedral approximant is $\text{Al}_{62.8}\text{Cu}_{26}\text{Fe}_{11.2}$ [14]. The transformation into the rhombohedral state is induced by a long annealing treatment (7 days at 700°C) of the as-quenched material [11]. X-ray-diffraction patterns of the two NMR samples show that they are single phased.

We have detected the Al spin echo in a fixed-field $H_0 = 6.996$ T in the temperature range [30,300 K] using pulsed NMR techniques (90° - 180° pulses). In the four samples the Al spectra exhibit a narrow line associated with the $m = -\frac{1}{2}$ to $m = +\frac{1}{2}$ nuclear spin transition, superimposed on a broad line (extending ≈ 3 MHz) due to the quadrupolar splittings of the four other nuclear spin transitions (see Fig. 1). The Al spectra are similar to those previously observed in other qc phases such as Al-Mn [15] or Al-Cu-V and Al-Cu-Mn [16]. They reflect a wide distribution of the local environments on the Al site. The quadrupolar effects on the Al site in the qc and approximant phases are indiscernible, which supports the idea of close local environments. In Al-Li-Cu the same conclusion was obtained in Ref. [17] for the Li site. No other phase was detected in the NMR spectra of the two Al-Cu-Fe samples, in agreement with diffraction data. The NMR spectra of the two Al-Li-Cu phases show the presence of Al metal. In the qc phase an additional Al resonance is observed (see Fig. 1), which in view of the diffraction data on the same sample is likely due to the Al nuclei in the T_1 phase. A huge advantage of the NMR technique by comparison with specific-heat experiments is

that non-single-phased samples can be meaningfully used as long as the other phases lead to resonances at quite different frequencies from the main one. The four spectra are temperature independent, which confirms the non-magnetic character of these phases. The presence of moments would have led to a broadening of the NMR line as the temperature decreases following the increase of the magnetization, as seen, for example, in qc Al-Mn [18] and qc Al-Cu-Mn [16].

T_1 was determined at the frequency ν_m of the maximum spin-echo intensity through the recovery of the nuclear magnetization $M_z(t)$ along the field direction z after the application at time $t=0$ of a radio-frequency saturation pulse saturating the $\frac{1}{2} - \frac{1}{2}$ transition. In order to normalize the data, we have plotted $f(t) = [M_e - M_z(t)]/[M_e - M_z(0)]$ as a function of the time, where M_e is the equilibrium magnetization. The saturation pulse length was adjusted such that $M_z(0) \approx 0$. A pulse slightly longer than the 90° pulse was necessary. We checked that $f(t)$ did not depend on the saturation pulse length when changed by $\pm 50\%$ around its optimal value. Typical relaxation curves are shown in Fig. 2. They do not follow a single exponential law e^{-t/T_1} . One reason is the presence of quadrupolar splittings. For a nuclear spin $\frac{3}{2}$,

$$f(t) = \alpha e^{-t/T_1} + \beta e^{-6t/T_1} + \gamma e^{-15t/T_1}, \quad (1)$$

with $\alpha + \beta + \gamma = 1$ [19]. Another reason could be the existence of a T_1 distribution. This would not be surprising in materials with a large number of distinct sites. In order to avoid these difficulties we have plotted all the data obtained at the various temperatures, for a given sample, as a function of the product tT of the time multiplied by the temperature. For each sample all the points merge nicely on a unique curve, as can be seen in Figs. 3 and 4,

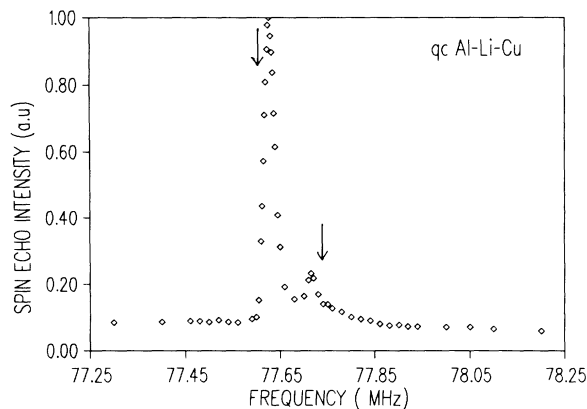


FIG. 1. NMR spin-echo intensity as a function of frequency, at 300 K, in the qc $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$ phase. The arrows indicate the reference position of the ^{27}Al resonance ($\nu_0 = 77.6063$ MHz) and the resonance frequency in Al metal (77.7336 MHz) in the applied field.

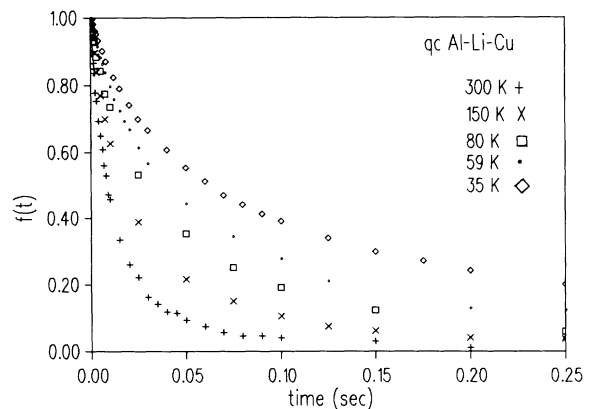


FIG. 2. Recovery of the nuclear magnetization $M_z(t)$ as a function of time in the qc $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$ phase, at several temperatures between 300 and 35 K, after the application at time $t=0$ of a pulse destroying the equilibrium magnetization M_e . We have plotted $f(t) = [M_e - M_z(t)]/[M_e - M_z(0)]$ vs t .

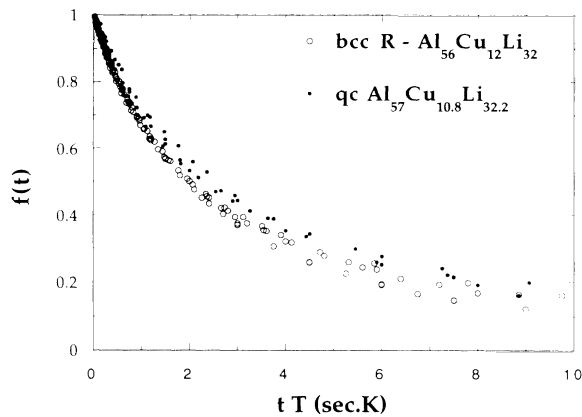


FIG. 3. $f(t)$ vs the product tT of the time multiplied by the temperature, for the qc $\text{Al}_{57}\text{Cu}_{10.8}\text{Li}_{32.2}$ phase. The data are those of Fig. 2. For the sake of clarity we have used the same symbol (\bullet) for all the data collected at different temperatures. The results for the bcc R $\text{Al}_{56}\text{Cu}_{12}\text{Li}_{32}$ phase are also shown (\circ).

which shows therefore the validity of a Korringa law (T_1T constant) in the investigated temperature range [30,300 K]. This demonstrates that the nuclear relaxation is dominated by the conduction electrons in the four samples. In qc Al-Li-Cu the observation of the Li resonance in the range [77,300 K] already led Lee *et al.* [17] to that conclusion. In Al-Li-Cu, the relaxation curves measured in the qc and approximant phases, although very similar, exhibit a small difference, larger than the error bars (Fig. 3). The relaxation is about 15% slower in the qc phase. The difference, if any, between the qc and approximant phases of Al-Cu-Fe lies within the error bars (Fig. 4). By comparing Figs. 3 and 4, it clearly appears that the relaxation is ≈ 3 times slower in Al-Cu-Fe than in Al-Li-Cu.

In a metal the NMR line is observed at a frequency ν higher than the resonance frequency in the applied field ν_0 . The Knight shift $K = (\nu - \nu_0)/\nu_0$ due to the coupling of the nuclei with the s conduction electrons is equal to $(8\pi/3)\chi_p\langle|\psi|^2\rangle_{\text{FS}}$, where $\chi_p = \mu_B^2 N(E_F)$ is the Pauli susceptibility per atom and $\langle|\psi|^2\rangle_{\text{FS}}$ is the square of the s -wave function at the nucleus averaged over those electrons at the Fermi surface (FS), while $(T_1T)^{-1}$ is proportional to $\langle|\psi|^2\rangle_{\text{FS}}^2 N^2(E_F)$. In Al metal $T_1T = 1.8$ sK. We can immediately note that our four samples are characterized by much slower relaxations. The $\pm \frac{1}{2}$ lines being symmetrical, we have neglected the eventual anisotropy of the Knight shift tensor and used the frequency of the maximum of the spin-echo intensity ν_m to calculate the shifts. The $K=0$ position was deduced from the observation of the Al metal resonance ($K = 1.64 \times 10^{-3}$) [20] in the same field. In crystalline and qc Al-Cu-Fe alloys the shifts nearly coincide, within the experimental resolution, and are both close to zero ($K \leq 10^{-4}$). Small positive values are observed in Al-Li-Cu alloys,

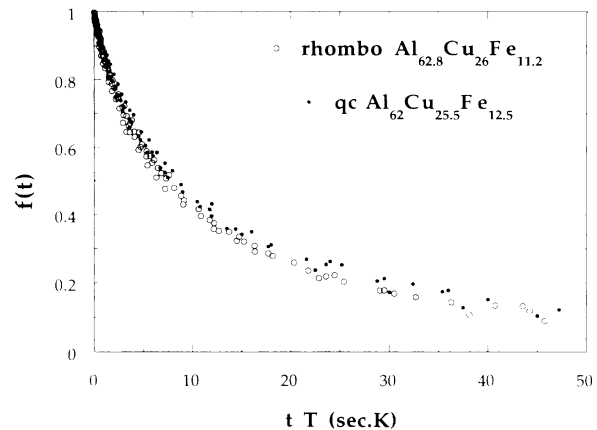


FIG. 4. $f(t)$ vs the product tT , for the quasicrystalline $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ phase (\bullet) and for the rhombohedral $\text{Al}_{62.8}\text{Cu}_{26}\text{Fe}_{11.2}$ phase (\circ).

$K = (0.34 \pm 0.034) \times 10^{-3}$ in the R phase and $K = (0.26 \pm 0.034) \times 10^{-3}$ in the qc phase. As expected there is a correlation between the K values and the relaxation effects (the smaller the K , the slower the relaxation). However, going further is difficult. The small measured shifts certainly include other contributions than that of the conduction electrons, especially the chemical shift, which are negligible in the case of Al metal. Moreover, the extraction of T_1T values from the data in Figs. 3 and 4 turns out to be difficult although good fits with Eq. (1) can be obtained. For Al-Cu-Fe, $T_1T = 60$ sK, with $\alpha = 0.25$, $\beta = 0.47$, and $\gamma = 0.28$. For Al-Li-Cu, $\alpha = 0.19$, $\beta = 0.34$, and $\gamma = 0.47$, with $T_1T = 26$ sK in the qc phase and $T_1T = 22$ sK in the R phase. But these α, β, γ values do not correspond to the expected values [19]. This discrepancy suggests a T_1 distribution and the values quoted above should only be taken as indicative.

As the qc and the approximant are thought to be built with the same structural units [8,9], it is very reasonable to assume that the s - p hybridization is the same in the two phases. The comparison of the T_1T values then allows a direct comparison of the $N(E_F)$ values. Our results therefore show that the densities of states at the Fermi level are indiscernible within a few percent in the crystalline and qc phases of Al-Cu-Fe. In Al-Li-Cu a small decrease of the $N(E_F)$ (about 7%) is observed in the qc phase, with respect to the approximant. Using the known $N(E_F)$ values in the two qc phases, as deduced from specific-heat data [1-3], we can conclude that reduced densities of states at the Fermi level also exist in the approximant phases. As the two qc phases have similar $N(E_F)$, the higher T_1 measured in Al-Cu-Fe alloys must reflect a decrease of the s character of the wave function on the Al site with respect to the case of Al-Li-Cu alloys.

In conclusion, the existence of a pseudogap at the Fermi level is not a specific property of the stable quasicrystalline alloys. The observation of a pseudogap in the R

Al-Li-Cu phase is actually in agreement with recent band calculations [21] and theoretical argument [6]. We found that only a small deepening of the pseudogap occurs in the qc Al-Li-Cu with respect to the approximant. In view of this result we may suggest that the spectacular changes of the transport properties between the R and qc phases [1] are mainly due to a reduced mobility of the electrons in the quasiperiodic structure, rather than to $N(E_F)$ effects. In Al-Cu-Fe no difference can even be detected between the qc and approximant phases, within our experimental accuracy. It should be emphasized that the rhombohedral Al-Cu-Fe phase is a high-order approximant of the qc structure, i.e., obtained by a small rotation of the cut, whereas the R phase is an approximant of lower order. Band-structure calculations, in the case of Al-Zn-Mg alloys [22], indicate a deepening of the pseudogap as the period of the approximant increases. The present results seem to validate this conclusion. Coming back to Hume-Rothery type of argument, we must conclude that crystalline approximant phases are already stabilized by their electronic properties. A further stabilization could occur in the qc phases, due to the quasiperiodicity, but in any case the involved energy differences must be very small.

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- [1] K. Kimura, H. Iwahashi, T. Hashimoto, S. Takeuchi, U. Mizutani, S. Ohashi, and G. Itoh, *J. Phys. Soc. Jpn.* **58**, 2472 (1989).
 - [2] B. D. Biggs, Y. Li, and S. Poon, *Phys. Rev. B* **43**, 8747 (1991).
 - [3] T. Klein, C. Berger, D. Mayou, and F. Cyrot-Lackmann, *Phys. Rev. Lett.* **66**, 2907 (1991).
 - [4] B. D. Biggs, S. J. Poon, and N. R. Munirathnam, *Phys. Rev. Lett.* **65**, 2700 (1990).
 - [5] A. P. Smith and N. W. Ashcroft, *Phys. Rev. Lett.* **59**, 1365 (1987).
 - [6] J. Friedel, *Helv. Phys. Acta* **61**, 538 (1988).

- [7] J. L. Wagner, B. D. Biggs, and S. J. Poon, *Phys. Rev. Lett.* **65**, 203 (1990).
- [8] V. Elser and C. Henley, *Phys. Rev. Lett.* **55**, 2883 (1985).
- [9] M. Audier, C. Janot, M. De Boissieu, and B. Dubost, *Philos. Mag. B* **60**, 437 (1989).
- [10] F. Dénoyer, G. Herger, M. Lambert, M. Audier, and P. Guyot, *J. Phys. (Paris)* **51**, 651 (1990).
- [11] D. Gratias, Y. Calvayrac, J. Devaud-Repski, F. Faudot, M. Harmelin, A. Quivy, and P. A. Bancel, Fourth International Conference on Quasicrystals, St. Louis, 1992 (to be published).
- [12] M. Bessière, A. Quivy, S. Lefebvre, J. Devaud-Rzepski, and Y. Calvayrac, *J. Phys. I (France)* **1**, 1823 (1991).
- [13] M. De Boissieu, C. Janot, J. M. Dubois, M. Audier, and B. Dubost, *J. Phys. Condens. Matter* **3**, 1 (1991).
- [14] The rhombohedral approximant studied here is not the alloy studied, for example, by Biggs, Li, and Poon in Ref. [2], which has the composition $Al_{63.5}Cu_{24.5}Fe_{12}$ and has been obtained by annealing 3 h at 760 °C, and then ≈ 24 h at 600 °C, the as-quenched material. As shown in [12], such a sample, although called rhombohedral by the authors of [2], is still in a (imperfect) quasiperiodic state. The only modification induced by the annealing at 600 °C is the occurrence of shoulders around the icosahedral Bragg peaks. These diffraction effects may correspond to the beginning of a transformation towards an approximant structure, closely related to the i phase. However, this very partially transformed state remains structurally imperfect and ill defined.
- [15] W. W. Warren, H. S. Chen, and G. P. Espinosa, *Phys. Rev. B* **34**, 4902 (1986).
- [16] T. Shinohara, A. P. Tsai, and T. Masumoto, *J. Mater. Res.* **7**, 62 (1992).
- [17] C. Lee, D. White, B. H. Suits, P. A. Bancel, and P. A. Heiney, *Phys. Rev. B* **37**, 9053 (1988).
- [18] H. Yasuoka, A. Soyoma, K. Kimura, and S. Takeuchi, *J. Phys. Soc. Jpn.* **55**, 1058 (1986).
- [19] A. Narath, *Phys. Rev.* **162**, 320 (1967).
- [20] G. C. Carter, L. H. Bennett, and D. J. Kahan, in *Metallic Shifts in NMR*, Progress in Materials Science Vol. 20, edited by B. Chalmers and W. Hume-Rothery (Pergamon, New York, 1977).
- [21] T. Fujiwara and T. Yokokawa, *Phys. Rev. Lett.* **66**, 333 (1991).
- [22] J. Hafner and M. Krajčí, *Phys. Rev. Lett.* **68**, 2321 (1992).