

Mössbauer spectroscopy of quasicrystals

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A critical review is presented of the application of Mössbauer spectroscopy in the study of quasicrystals. The importance of a correct analysis of the Mössbauer spectra is emphasized. Current progress associated with Mössbauer studies of quasicrystals is discussed. The urgency for theoretical calculations of the distributions of quadrupole splittings for various possible structural models of quasicrystals is stressed. Suggestions for future work are given.

1. Introduction

Until recently, it was believed that solids could either be crystalline or amorphous. The discovery by Shechtman et al. [1] extended this dichotomous classification by introducing the notion of quasicrystals (QCs) – a form of matter exhibiting classically forbidden symmetries (icosahedral, octagonal, decagonal, and dodecagonal). A current problem in condensed matter physics is to determine how this quasiperiodic structure affects various physical properties. It is expected that quasiperiodicity should lead to some exotic physical properties found neither in crystalline nor in amorphous alloys [2].

The main thrust of research has been directed at elucidating the complex atomic structure of QCs, mainly the icosahedral (*i*) and decagonal (*D*) alloys. In spite of a torrent of structural investigations, it is still not clear which of major competing structural models [3] is the most appropriate for QCs. Additionally, within a given structural model, the problem of the actual arrangement of atoms remains unsolved.

Mössbauer spectroscopy (MS) and other local probes should, in principle, be useful in elucidating structural aspects and other properties of QCs. Unfortunately, due to methodological problems in the spectral analysis and/or because of the use of multi-phase samples, MS has had a smaller impact in studies of QCs than was expected.

The aim of this paper is to critically review the contribution of MS in studies of some physical properties of nonmagnetic and magnetically ordered QCs. Emphasis is placed on the proper analysis of Mössbauer spectra resulting from distributions of hyperfine parameters. This is essential if the parameters extracted are to have

physical meaning. Some general trends in hyperfine parameters of QCs and their relation to the structural and magnetic properties of QCs are presented. Finally, some topics for future MS research on QCs are suggested.

2. Mössbauer spectroscopy results and interpretation

2.1. NONMAGNETIC QUASICRYSTALS

Mössbauer spectra of almost all nonmagnetic QCs consist of two very broad and structureless lines, and are similar to the spectra of amorphous alloys. These spectra can be analyzed at two levels of sophistication.

If only average values of the isomer shift δ and the quadrupole splitting Δ are of interest, then a simple fit with, for example, an asymmetric Lorentzian doublet is sufficient. The values of $\bar{\delta}$ and $\bar{\Delta}$ determined in this way have a relative error of less than a few percent. Increasing the number of fitted component doublets (two doublets usually suffice) significantly improves the fit and the resulting $\bar{\delta}$ and $\bar{\Delta}$ values are determined more precisely. A danger here, however, lies in the temptation to uncritically associate the component doublets with specific "sites" in QCs which, as is discussed below, led to the now discredited two-site model.

At another level of spectral analysis, one attempts to derive the distribution of quadrupole splittings $P(\Delta)$ which is closest to the true one. A perusal of MS literature associated with the derivation of $P(\Delta)$ from the Mössbauer spectra of nonmagnetic disordered materials creates an impression that the derived $P(\Delta)$ is method dependent, and thus unreliable. It is argued here that the apparent unreliability of the derived $P(\Delta)$ is a consequence of the uncritical use of a given, in principle reliable, method of spectral analysis and not of the method itself (a review of various methods of spectra analysis in terms of $P(\Delta)$ can be found, for example, in refs. [4] and [5]).

One obtains a rather limited insight into the structural properties of QCs by analyzing only the average values $\bar{\delta}$ and $\bar{\Delta}$. This is due to the fact that $\bar{\delta}$ and $\bar{\Delta}$ do not change significantly in metallic systems of different structures. For example, the $\bar{\Delta}$ values for amorphous, *i*, and crystalline forms of the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy are, respectively, 0.50(1), 0.38(1), and 0.41(1) mm/s [6]. The corresponding $\bar{\delta}$ values (relative to α -Fe) are 0.26(1), 0.24(1), and 0.23(1) mm/s [6].

It is the derived distribution $P(\Delta)$ for a given QC which is of great importance since it reflects the local atomic structure around a Mössbauer atom. This distribution should then be compared with the one calculated for different plausible structural models. Unfortunately, such theoretical distributions are yet to be calculated. Their unavailability reflects the inherent difficulties associated with calculations of the electric field gradient tensor in crystalline metallic systems, which are compounded in disordered metallic systems such as QCs or amorphous alloys. A good starting point could be the calculations of $P(\Delta)$ in crystalline approximants of QCs. The lack of theoretically predicted $P(\Delta)$ also limits the great potential of MS as a complementary method to diffraction methods in solving structural problems of disordered materials.

2.1.1. Two-site model

MS was applied for the first time to the $i\text{-Al}_6(\text{Mn}_{1-x}\text{Fe}_x)_{1.03}$, with $x = 0.15$ and 0.38 , by Swartzendruber et al. [7]. These authors fitted the spectra with two symmetric quadrupole doublets whose intensity ratio was *constrained* to the golden mean $\tau = 1.618$. They associated the pair of doublets with “two kinds of asymmetric sites for the transition metal atoms” and interpreted the successful fit as evidence (which was soon taken as an experimentally established fact [8]) of the icosahedral quasicrystal model for $i\text{-Al-Mn}$ alloys. A two-doublet analysis, without any constraint on the intensity ratio of component doublets, has been widely used in MS studies of other i alloys [9–13] and D alloys [10, 14, 15], in spite of the fact that, as early as 1986, Eibschütz et al. [16] showed the superiority of a fit based on a distribution of sites. The justification of such a fit was the presence of two broad lines in the Mössbauer spectra of i alloys. A two-doublet fit, referred to as a two-site model [11], was associated with “the existence of two distinct transition-metal sites” [11] in i alloys.

The two-doublet fit of Mössbauer spectra of i and D alloys is methodologically incorrect, as has been discussed in detail [17]. We summarize the situation below.

First, the Mössbauer spectra of nonmagnetic QCs are in the form of two smooth and broad quadrupole lines with no apparent structure. A fit of such spectra with *any* model must account for the linewidth Γ of the component subspectra used, which typically should not be broader than about $0.24(2)$ mm/s [17]. The failure to give such an account may result in mathematically excellent fits, as is usually the case with the two-doublet fits [9, 17], with Γ values of component doublets still unacceptably large. Generally, Γ of one doublet is still large, whereas Γ of another doublet is close to the expected value of $0.24(2)$ mm/s, or sometimes even smaller than Γ_{nat} (see table 1 in [18]), which is clearly unphysical. Parameters derived from such fits, and any conclusions which are based on them, are meaningless.

To illustrate this, a Mössbauer spectrum of a single-phase amorphous alloy $(\text{Fe}_{0.1}\text{Ni}_{0.9})_{77}\text{Si}_{10}\text{B}_{13}$ is fitted first with an asymmetric doublet (fig. 1(a)). As expected, a bad fit is obtained, as evidenced by the misfit at the shoulders and in the central part of the spectrum. A relatively good fit in a mathematical sense can be obtained by fitting the spectrum with two symmetric doublets in one of two ways: either with two different values of δ and two similar values of Δ (fig. 1(b)), or with two similar values of δ and two different values of Δ (fig. 1(c)). Method (b), which was used to fit the spectra of $i\text{-Al-Cr-Fe}$ alloys [11], is additionally unjustified since it is well established that the relative range of changes in δ in metallic crystalline alloys with distinct crystallographic sites is much narrower than the relative range of changes in Δ . The values of Γ of component doublets for method (b) are $0.362(5)$ and $0.312(7)$ mm/s, whereas these values for method (c) are $0.364(7)$ and $0.304(8)$ mm/s.

It is clear that relatively good fits are obtained with two doublets characterized by large values of Γ (fig. 1). It would, however, be false to conclude on the basis of such fits that there are two distinct Fe sites in the amorphous $(\text{Fe}_{0.1}\text{Ni}_{0.9})_{77}\text{Si}_{10}\text{B}_{13}$ alloy.

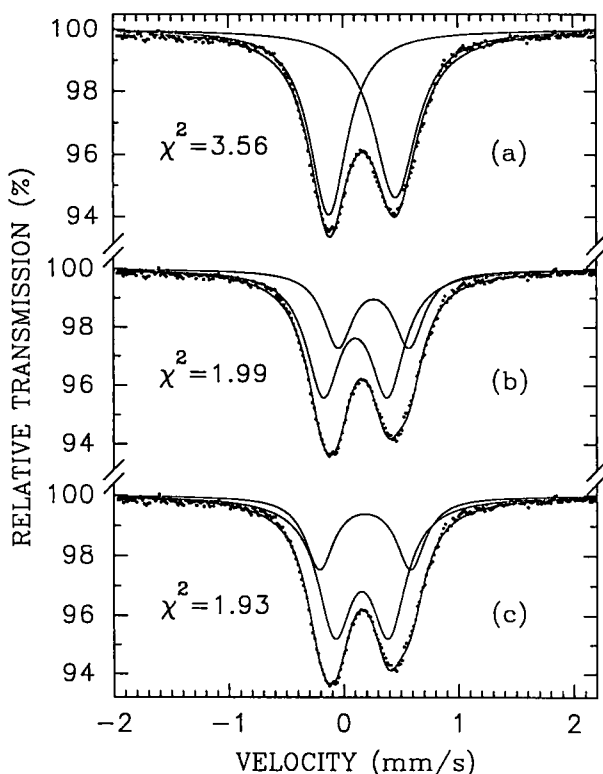


Fig. 1. ^{57}Fe Mössbauer spectrum of amorphous $(\text{Fe}_{0.1}\text{Ni}_{0.9})_{77}\text{Si}_{10}\text{B}_{13}$. The solid line is a least-squares fit to an asymmetric doublet (a) and to two symmetric doublets (b) and (c), as described in the text. The component doublets are also shown. The velocity scale is relative to $\alpha\text{-Fe}$ and the values of the reduced chi-square χ^2 are indicated.

Second, the paramagnetic spectra of some inorganic compounds (for instance, mixed spinels [19]), in which Fe atoms are known to be at two distinct crystallographic sites with a non-zero electric field gradient [19], are also in the form of two broad and structureless lines. Although good fits of such spectra can be obtained with two doublets characterized by unphysically broad lines, the parameters of the doublets are meaningless in determining, for example, the cation distribution. The latter can be determined from the spectra below the ordering temperature, where the contributions from the two sites are usually clearly separated [19]. Thus, even in some materials in which Fe atoms do occupy two crystallographically distinct sites, the fits of paramagnetic Mössbauer spectra with two doublets cannot be used to derive any physically meaningful information.

Third, the analysis of the in-field Mössbauer spectra of *i* alloys convincingly demonstrated [20, 21] the incorrectness of the two-doublet analysis. It is thus concluded

that the values of hyperfine parameters associated with the two component doublets of Mössbauer spectra of *i* and D alloys [9–15] have no physical meaning and the conclusion of there being two distinct transition-metal sites in QCs is unfounded. The large line broadening observed in the Mössbauer spectra of QCs reflects the presence of a multiplicity of sites; we discuss this below.

Very recently, Eibschütz et al. [22] have reported Mössbauer spectra of $D\text{-Al}_{65}\text{Cu}_{15}\text{Co}_{20-x}\text{Fe}_x$, with $x = 0.1$ and 0.5 . The spectrum presented exhibits a clear structure which the authors used as evidence of two narrow distributions of iron sites. They also presented an atomically decorated prismatic Penrose-tile model of the D phase, which was interpreted to be compatible with the measured spectra [22].

2.1.2. Quadrupole splitting distributions

As mentioned above, Eibschütz et al. [16] were the first to recognize that the Mössbauer spectra of *i* alloys can be fitted correctly only with a distribution of quadrupole splitting magnitudes, which is equivalent to the presence of a multiplicity of transition-metal sites. In retrospect, this conclusion does not seem to be unexpected in view of the fact that a quasicrystal by its very nature has an infinite number of distinct crystallographic sites [23].

Once the necessity of the analysis in terms of $P(\Delta)$ has been recognized, the task now is to derive $P(\Delta)$ as closely as possible to the true distribution, and next to compare it with the distributions calculated for different possible models of the atomic structure. There are generally two main approaches used to extract $P(\Delta)$: (a) either a specific shape of $P(\Delta)$ is assumed (for example, a shell model [16], originally suggested by Czjzek et al. [24] for amorphous alloys) and the parameters characterizing this shape are obtained from the fit, or (b) no a priori assumption about the shape of $P(\Delta)$ is made (usually the constrained version [25] of the Hesse–Rübartsch method [26] or a new method recently introduced by Rancourt and Ping [5] are used [27]). The disadvantage of approach (a) is that it presupposes the shape of $P(\Delta)$, which may differ considerably from the real $P(\Delta)$. The potential disadvantage of approach (b) is its sensitivity to some parameters fixed in the fit and which must be chosen arbitrarily; if this choice is done uncritically, this may lead to artifacts in the derived distribution $P(\Delta)$. However, it seems preferable to use approach (b) since it does not restrict $P(\Delta)$ to a specific family of shapes. The asymmetry of the experimental spectra is taken into account by assuming a linear relation $\delta = \delta_0 + a\Delta$, where δ_0 and a are fitted parameters. This relation is based on the observation that generally δ and Δ are proportional to each other in inorganic systems.

Whereas approach (a) mentioned above, and also the method described in [5,27], do not require fixing any parameters in the fit, the Le Caër–Dubois [25] method does. In particular, it requires fixing the linewidth Γ of component doublets, choosing the number of discrete steps n , etc. This method should be applied to

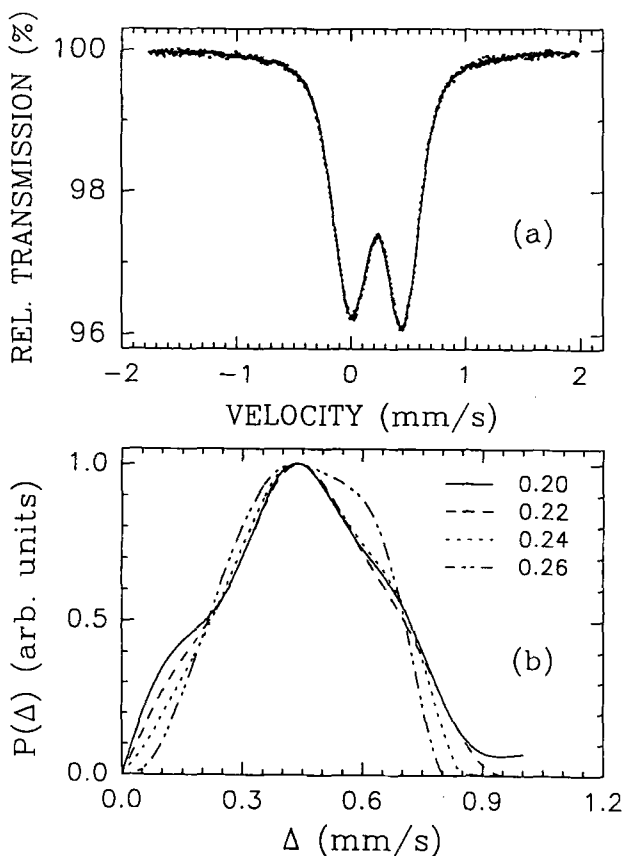


Fig. 2. (a) ^{57}Fe Mössbauer spectrum of icosahedral $\text{Al}_{86}\text{Cr}_8\text{Fe}_6$ fitted (solid line) using the Le Caër–Dubois method [25] for the linewidth Γ corresponding to the minimum of χ^2 in fig. 3. The velocity scale is relative to $\alpha\text{-Fe}$. (b) Distributions $P(\Delta)$ corresponding to different values of Γ (in mm/s) used in the fit of the spectrum in (a) with the Le Caër–Dubois method.

statistically good quality spectra. If the values of the fixed parameters are not chosen properly and/or this method is applied to statistically poor quality spectra, then unphysical features appear in $P(\Delta)$ which are difficult to distinguish from the possible real features (see, for example, fig. 4 in [28]). A significant sensitivity of the shape of $P(\Delta)$ extracted from the Mössbauer spectrum of $i\text{-Al}_{86}\text{Cr}_8\text{Fe}_6$ [29] (fig. 2(a)) on the value of Γ used in the Le Caër–Dubois method is illustrated in fig. 2(b), and the dependence of the reduced chi-square χ^2 on Γ is shown in fig. 3 (the value of n was 24; larger values of n lead to unphysical oscillations in $P(\Delta)$). It is thus concluded that the choice of Γ in the Le Caër–Dubois method should be based on the minimum of χ^2 rather than on the value obtained either from a spectrometer calibration with an $\alpha\text{-Fe}$ or chosen arbitrarily [28].

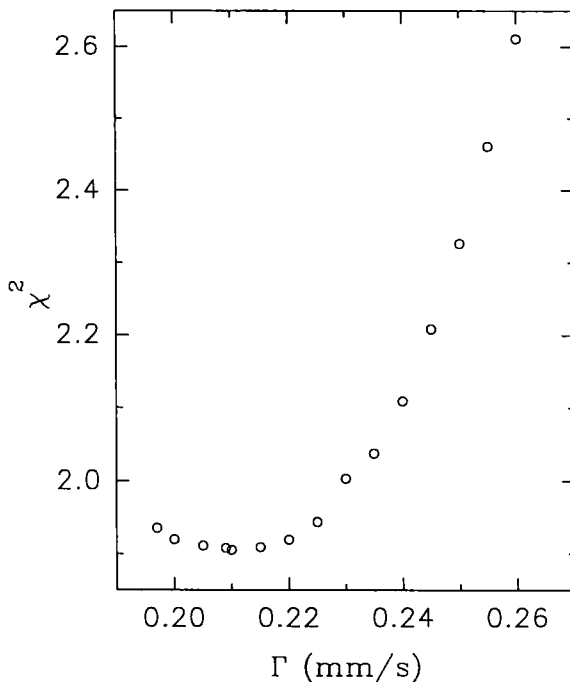


Fig. 3. Dependence of χ^2 on Γ for the fits of the spectrum in fig. 2(a) with the Le Caër–Dubois method [25].

The distributions $P(\Delta)$ extracted from the fits of the spectrum in fig. 2(a) using the shell, Le Caër–Dubois, and Rancourt–Ping methods are compared in fig. 4. The corresponding Γ values are 0.232(2), 0.210(5), and 0.209(1) mm/s, whereas the χ^2 values are 3.626, 1.906, and 1.888. It is worth noticing that the Γ values obtained using the Le Caër–Dubois and Rancourt–Ping methods are very similar, as is expected for the thin absorber used [29]. The relatively high value of χ^2 obtained for a shell model indicates that this model cannot properly account for the shape of the spectrum of the studied *i* alloy. This is not surprising if one notices that the shell model was designed to account for the shape of $P(\Delta)$ in amorphous alloys [24]. Although the χ^2 values are essentially the same for the fits with the two other methods [5,25] (by decreasing n in the Le Caër–Dubois method, one can obtain the same χ^2 as in the Rancourt–Ping method), the shapes of $P(\Delta)$ differ (fig. 4). This demonstrates the limitations inherent to zero-field MS.

The shape of the derived $P(\Delta)$ can be influenced by the sample texture, the Goldanskii–Karyagin effect, or the possible distribution of the isomer shifts $P(\delta)$. The influence of the first two effects has yet to be studied. The distribution $P(\delta)$ is expected to be very narrow [3] since the changes of δ upon crystal structure are

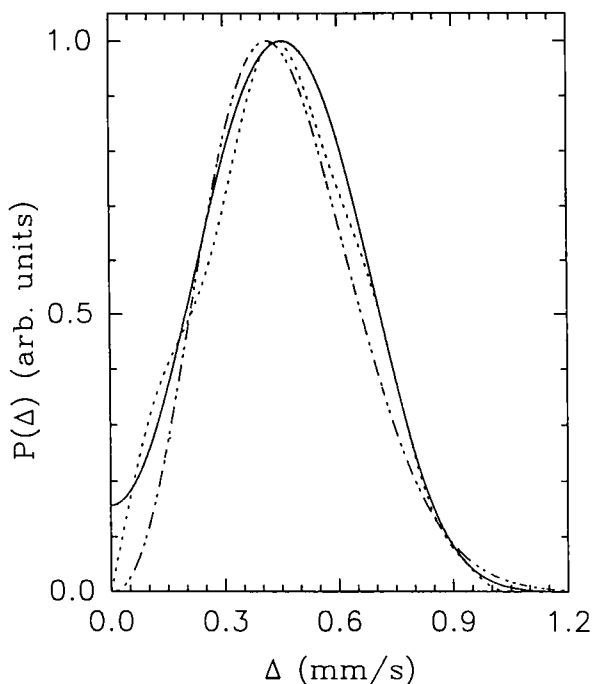


Fig. 4. Distributions $P(\Delta)$ obtained from the fits of the spectrum in fig. 2(a) using the shell model (dash-dot-dot line), the Rancourt-Ping method (solid line), and the Le Caër-Dubois method (dot line).

rather small in crystalline metallic systems. Therefore, its influence on $P(\Delta)$ should be very small.

It has sometimes been argued that the distribution $P(\Delta)$ derived from the spectra of *metastable* i alloys is not a direct consequence of quasiperiodicity, but rather results from strains present in a sample and induced during the process of the sample preparation. It was therefore very significant that this distribution exists also in the high-quality (as judged by the widths of X-ray diffraction lines [2]) *stable* i alloys $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ [17, 30–32]. This fact constitutes important Mössbauer evidence of intrinsic disorder present in i alloys, which is not seen in X-ray diffraction spectra where the narrowest linewidth for the best i -Al-Cu-Fe alloys is limited by the resolution of a spectrometer [2].

In a recent work, Nasu et al. [32] have demonstrated how MS has interesting applications in monitoring the transition from the i to amorphous structure in the $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ alloy. Their analysis, among other things, shows the increase of $\bar{\delta}$ with $\bar{\Delta}$, which constitutes additional justification for the use of a linear relation $\delta = \delta_0 + a\Delta$ in the fits of Mössbauer spectra exhibiting the distribution of the electric quadrupole interactions.

2.1.3. In-field Mössbauer spectroscopy

Due to the nature of the $3/2 \rightarrow 1/2$ Mössbauer transition in ^{57}Fe , zero-field spectra provide only the distribution of the absolute values of the quadrupole splitting $\Delta = \frac{1}{2} eV_{zz}Q(1 + \eta^2/3)^{1/2}$. However, for discriminating between possible models of a local atomic structure, the distributions of both V_{zz} and η are required, as was successfully demonstrated for amorphous alloys [33]. Such distributions, in principle, can be extracted from in-field Mössbauer spectra.

A summary of in-field MS results for QCs is presented in table 1. They indicate a preponderance of the negative values of V_{zz} in *i* alloys, whereas for D alloys the majority of the V_{zz} values seems to be positive. A detailed analysis of the in-field spectra of *i*-Al-Si-Mn(Fe) and corresponding crystalline alloys showed

Table 1

Parameters for *i* and D quasicrystals extracted from the in-field Mössbauer spectra.
 p_- is the fraction of Fe atoms with a negative sign of V_{zz} ($p_+ = 100 - p_-$).

Sample	Predominant sign of V_{zz}	p_- (%)	η	Ref.
<i>i</i> -Al _{4.3} Si _{0.06} (Mn _{0.72} Fe _{0.28})	< 0	63	0.6	[20, 34]
<i>i</i> -Al ₇₂ Si ₆ (Mn _{1-x} Fe _x) ₂₂ $x = 0.01$ and 0.25	< 0	80	0.6	[35, 36]
<i>i</i> -Al ₈₄ Si ₁ (Mn _{0.72} Fe _{0.28}) ₁₅	< 0	70.3	0.6	[21]
<i>i</i> -Al ₇₉ (Mn _{1-x} Fe _x) ₂₁ $x = 0.25$ and 0.50	< 0		0.6	[37]
<i>i</i> -Al ₈₀ (Mn _{0.72} Fe _{0.28}) ₂₀	< 0	54.8	0.6	[21]
<i>i</i> -Al _{4.44} Si _{0.06} (Cr _{0.5} Fe _{0.5})	< 0	53	0.6	[20, 34]
<i>i</i> -Al ₈₂ Si ₁ (Cr _{0.5} Fe _{0.5})	< 0	60.9	0.6	[21]
<i>i</i> -Al ₆ Cr _{0.7} Fe _{0.3}	> 0 ^{a)}		0.8–0.9	[38]
<i>i</i> -Al ₆₅ Cu ₂₀ Fe ₁₅	< 0	59	0.8	[31]
D-Al ₇ (Mn _{0.7} Fe _{0.3}) ₂	> 0 ^{a)}		0.7–0.8	[38]
D-Al ₈₀ (Mn _{0.72} Fe _{0.28}) ₂₀	> 0	49.8	0.6	[21]

^{a)} Suggested by the shape of the fitted spectrum.

similarities in the local order between these *i* alloys and the hexagonal phase Al₇₄Si₆(Mn_{0.72}Fe_{0.28})₂₀ [21]. The large value of η (table 1) can be interpreted as evidence of disorder inherent to QCs. It also excludes the presence of sites with cylindrical symmetry. The closeness of p_- and p_+ in D alloys (table 1) seems to indicate the presence of larger disorder in D than in *i* alloys. Unfortunately, the lack

of serious theoretical studies connecting various possible structural models of QCs with the Mössbauer parameters and the distributions $P(\Delta)$ derived from zero-field and in-field spectra significantly reduces the usefulness of MS in studies of the structural properties of QCs.

In-field MS turned out to be very useful [35, 37, 39] in providing a convincing experimental argument for the notion of two separate *classes* of Mn(Fe) sites in paramagnetic *i*-Al–Mn–Si alloys. These classes are distinguished by the presence or absence of a localized moment, as has been discussed in detail [17]. It was later shown that two such classes of sites also exist in magnetic *i*-Al–Ge–Mn and Al–Cu–Ge–Mn alloys [40, 41].

2.2. MAGNETIC QUASICRYSTALS

Diamagnetism, paramagnetism, and spin-glass behaviour have been observed in many QCs [17]. Recently, it was claimed that ferromagnetism was observed in *i*-Al–Fe–Ce, Al–Ge–Mn, Al–Cu–Ge–Mn, and Si-rich Al–Mn–Si alloys (see references in [40]). The unusual property of this apparent ferromagnetism is its small magnetization and comparatively high Curie temperatures T_c . This suggests that it may be due, at least partially, to small amounts of magnetically ordered impurities [40].

Mössbauer spectra of $\text{Al}_{65}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}\text{Mn}_{25}$, with $x = 3, 6,$ and 10 measured at room temperature [42–44] and at 110 K for $x = 3$ [42], were fitted using first-order perturbation theory (FOPT) to either a simple six-line Zeeman pattern [42] or using the Le Caër–Dubois method to derive the distribution $P(H_{\text{hf}})$ of the hyperfine magnetic fields H_{hf} . It was assumed [42, 44] that since the reported T_c for the composition $x = 0$ is 467 K, then Mössbauer spectra at $T < T_c$ must be due only to a magnetic dipole interaction M1, with an electric quadrupole interaction E2, which is very small (FOPT). A criticism of such an analysis has been given [40, 41, 45]. Based on an analysis of X-ray diffraction, differential thermal analysis, magnetization, and MS (at 4.2 and 295 K), it was shown [40, 41] that the apparent high T_c in *i*-Al–Cu–Ge–Mn and Al–Ge–Mn alloys results from the presence of a crystalline ferromagnetic second phase AlGeMn. It was suggested [40] that T_c of *i*-Al–Cu–Ge–Mn should not be much above 4.2 K (the upper limit of T_c was estimated to be 100 K [41]). This has recently been confirmed by Nasu et al. [46] who, by combining X-ray diffraction and MS over a wide temperature range, convincingly showed that there is a magnetic transition at 30 K in *i*- $\text{Al}_{65}\text{Cu}_{10-x}\text{Fe}_x\text{Ge}_{25}\text{Mn}_{25}$, with $x \leq 3$. This leads to the conclusion that the distributions $P(H_{\text{hf}})$ and other hyperfine parameters related to M1 interaction extracted from the spectra of *i*-Al–Cu–Ge–Mn alloys at 110 and 300 K [42–44, 47], which are presented as well established facts in a recent review on the magnetism of QCs [48], are in reality unphysical.

It is now generally recognized that there are two *classes* of transition-metal sites (not to be confused with the discredited two-site model discussed above) in paramagnetic QCs [17, 35, 37, 39]. The first experimental evidence for the presence of

such two classes in magnetically ordered i -Al–Mn(Fe)–Ge and Al–Mn–Cu(Fe)–Ge alloys has been presented in a recent MS study [40,41]. It has been shown [40,41] that the 4.2 K Mössbauer spectra could be analyzed in terms of nonmagnetic and magnetic components. Thus, the two classes of transition-metal sites seem to be intrinsic to both nonmagnetic and magnetic QCs studied so far. Evidence was also presented [41] that *very small* amounts of Fe atoms substitute randomly on transition-metal sites, whereas for larger concentration they preferentially enter the nonmagnetic class of sites.

The application of MS to magnetic QCs shows that extreme caution has to be exercised in the analysis of Mössbauer spectra since the available samples might contain small amounts of a second magnetic phase(s). It also shows that when a careful analysis of complex Mössbauer spectra is combined with the results obtained with other experimental techniques [40,41,46], then some definitive conclusions can be made about the magnetism of QCs.

3. Suggestions for future work

After the initial confusion associated with the two-site model resulting from a methodologically erroneous analysis of the paramagnetic Mössbauer spectra, the current studies aim at extracting a reliable $P(\Delta)$. This can only be achieved through a careful and critical analysis of Mössbauer spectra. High-quality in-field Mössbauer spectra of nonmagnetic QCs are of great importance, since the parameters derived from them are important in elucidating the unsolved problem of the atomic structure of QCs. There is an urgent need for theoretical calculations of $P(\Delta)$ and other relevant parameters associated with the E1 interaction for different possible models of the atomic structure of QCs. Calculations of $P(\Delta)$ for the crystalline approximants of QCs could be a good starting point. The present absence of such calculations significantly limits the great potential of MS in this area. Finally, MS should, whenever possible, be combined with other experimental techniques in studies of new magnetic QCs since the samples still cannot be produced at present as fully single phase.

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