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Investigation of Elementary Excitations in AlCuFe Quasicrystals by Means of Low-Temperature Specific Heat

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Abstract. — We report on an accurate low-temperature specific heat \( C_p \) study of several icosahedral AlCuFe samples of high structural quality in a broad \( 0.1 \leq T \leq 10 \) K temperature interval. The analysis shows deviations of \( C_p \) from the standard \( \gamma T \) and \( (\beta T^3 + \delta T^5) \) variations, generally well obeyed in crystalline (semi-)metallic alloys in this \( T \)-range for the electronic and phonon contributions respectively. We relate the unusual vibrational heat capacity to the very peculiar behaviour of vibrational states in quasicrystals, characterized by numerous dispersionless modes, broadened in energy, and extending down to low frequency. On the other hand, sub-linear variations of \( C_p \) at very low temperature, below 1 K, hint for the presence of another kind of excitations in addition to itinerant electrons.

Résumé. — Nous exposons une étude précise de la chaleur spécifique \( C_p \) d’échantillons icosahédriques AlCuFe de grande qualité structurale, dans la gamme étendue de température entre 0.1 et 10 K environ. L’analyse des résultats montre des déviations aux lois standards \( \gamma T \) et \( (\beta T^3 + \delta T^5) \), généralement bien observées dans cette gamme de température pour les contributions électronique et de réseau, dans le cas des alliages (semi-)métaalliques cristallins. Nous faisons la relation avec les propriétés vibrationnelles très spécifiques des quasicristaux, caractérisés par une forte densité de modes sans dispersion, élargis en énergie et s’étendant à basse fréquence. D’autre part, des variations sub-linéaires de \( C_p \) à très basse température, en dessous de 1 K, suggèrent la présence d’un autre type d’excitations que les électrons itinérants.

1. Introduction

Among unusual specific properties induced by the quasiperiodicity, those dealing with the density of states (DOS) of elementary excitations such as electrons, phonons or more generally vibrational excitations, have been the matter of intensive research [1]. Specific heat is one of

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the most convenient tool to obtain direct informations on the DOS of excitations and we will discuss here specific heat data in the special case of the AlCuFe icosahedral species. Indeed, this system appears up to now as the most suitable among thermodynamically stable quasicrystals (QC) of high crystallographic quality for the study of elementary excitations as electrons and phonons. The other species of similar high quality which are the most widely investigated by numerous techniques are AlPdMn, and more recently AlPdRe. However, the low-temperature specific heat $C_p$ of AlPdMn with Mn concentration between 8 and 9.5 at.%, which yields the highest crystallographic quality, is dominated below 5 K by a broad spin-glass anomaly due to a few percent of magnetic Mn atoms [2, 3], and in the case of AlPdRe, it is dominated below $\sim 1$ K by the nuclear hyperfine (electric quadrupolar) contribution of the Re nuclei [4, 5]. As we intend to demonstrate in the following, in order to carefully investigate both electronic and vibrational excitations, one needs experimental data over a wide $T$-interval, in particular extending well below 1 K for the definition of the “electronic” contribution.

We report on a study of a series of AlCuFe samples, icosahedral single-phased as verified by X-ray investigation; there is no contribution to $C_p$ originating either from magnetic ( electronic or nuclear) interactions, or from hyperfine nuclear quadrupolar terms, which extends above 0.15 K, and this allows a self-consistent analysis of $C_p$ only in terms of electronic and lattice contributions between 0.15 and 7 K or even 40 K for one sample.

From the present study and taking in account other data from the literature, we will conclude to an unconventional behaviour of the lattice heat capacity which deviates from the $T^3$ Debye regime at unexpected low temperatures, and rather obeys a power law as $T^{3.6}$ or $T^{3.9}$ over one decade of temperature. In addition, our data show deviations from a strictly linear $\gamma T$ variation for two samples in the low $T$-range ($T \lesssim 1$ K) where the heat capacity is dominated by the free electron contribution.

The organization of the paper is the following: after information about characterization of the samples and some experimental details in Section 2, we develop in Section 3 the analysis of the heat capacity investigated over the broad $T$-range from 70 mK up to 7 or 40 K. We successively discuss the possible temperature dependence regimes in the different $T$ intervals. In Section 4, we discuss the origin of the vibrational contribution on the basis of the very peculiar vibrational properties (propagating against localized modes) of the QC’s, demonstrated from the numerous results in inelastic neutron scattering techniques: phonon dispersion relations and vibrational density of states; and thereafter the origin of the “electronic” contribution, predominant in the $T$-range below 1 K.

2. Samples Characterization and Experimental Conditions

We have investigated 3 different samples in the composition range of high structural quality, in the form of large size polyquasicrystalline ingots, prepared by conventional casting at CECM-CNRS in Vitry (France), and subsequent long annealing to improve the structural quality. Two different samples of nominal composition Al$_{63}$Cu$_{23}$Fe$_{12}$ were issued from a same parent ingot, 300 g mass. Due to different thermal treatments for homogeneization, they can slightly differ in structural quality (amount of defects), homogeneity and composition (a maximum variation of 0.5 at.% Fe or Cu). An extensive structural investigation by X-ray diffraction for this composition is given in reference [6]. Although the Bragg peaks are sharp and all are indexed to the icosahedral group symmetry, the presence of weak shoulders at the foot (basis) of the peaks indicates that the icosahedral phase is not perfect: this broadening reveals the beginning of structural evolution towards the rhombohedral approximant, the physical properties of which are undistinguishable from the icosahedral phase. Indeed, for this nominal composition the equilibrium state at 700–750 °C corresponds to icosahedral + rhombohedral. A complete
transformation towards this equilibrium is impossible due to too small driving force, but a perfect icosahedral structure, defined by the absence of any shoulder at the Bragg peaks, can never be achieved for this composition, whatever is the annealing temperature [6, 7]. We will mention this composition as metastable icosahedral phase, by reference to its low temperature stability.

The first sample at this composition, referred as to AlCuFe12-(a) in the following, 0.389 g mass, was investigated by different techniques: electrical resistivity (with values; $\rho_{300K} = 2500 \mu \Omega$ cm or $\sigma_{300K} = 400 (\Omega \text{ cm})^{-1}$, resistivity ratio $\rho_{4K}/\rho_{300K} = 1.75$) [8]; the magnetic susceptibility, which indicates a purely diamagnetic behaviour, an intrinsic property of the pure i-AlCuFe system (Fig. 3 in Ref. [9]); and two different specific heat experiments, one in the $T$-range 1.5-12 K [10] and the second between 0.1 and 4 K with the present technique [11], which will be discussed later. X-ray diffraction on this sample clearly shows deformations of the Bragg peak profiles, similar to those already observed in reference [6] (Fig. 8) after annealing at 600 °C. In addition to the first magnetic study, a complete magnetization study using a very sensitive SQUID technique was done in CRTBT [12] which could detect a very slight paramagnetic contribution in addition to the predominant diamagnetic term, and which was ascribed to a fraction of $8 \times 10^{-5}$ of the total number of Fe atoms which are magnetic (with a spin $S = 2$).

The second one, referred to as AlCuFe12-(b), 2.70 g mass, was also characterized by X-ray powder diffraction: its pattern is very similar to that one already published in reference [6] (Fig. 8) for the same composition after annealing at 800 °C. The amplitude of the shoulders in the tails of the Bragg peaks is smaller than in sample (a), the structural state is closer to the ideal quasiperiodic phase. A resistivity measurement [13a] on a piece of this sample gives $\rho_{300K} = 2630 \mu \Omega$ cm (or $\sigma_{300K} = 350 (\Omega \text{ cm})^{-1}$), slightly higher than for sample (a), with almost the same resistivity ratio $\rho_{4K}/\rho_{300K} = 1.825$, values in excellent agreement with those published for samples of the same composition annealed at 800 °C [14, 15]. A magnetic investigation on a piece of the sample by the same sensitive magnetization technique as for sample (a) gives a fraction of $2 \times 10^{-4}$ of the total number of Fe atoms which are magnetic ($S = 2$).

A third sample has been studied, of composition Al62Cu25.5Fe12.5, 3.48 g mass, referred to as AlCuFe12.5. This composition corresponds to the perfect icosahedral structure, stable at every temperature, which is defined in a very narrow domain of composition [6, 7], as the structural ground state. Contrary to Al65Cu25Fe12, there is no broadening of the basis of the reflection peaks. Due to the large size of the sample, there remains in some parts very minute amounts of cubic $\beta$ phase. Otherwise, the X-ray diffraction pattern is similar to that published in reference [6]. The magnetic investigation shows an intermediate behaviour between the two previous samples, so that we can estimate a fraction of $\approx 1.5 \times 10^{-4}$ of the total Fe atoms which are magnetic ($S = 2$). Resistivity measurements [13b] on a piece of this sample are also in excellent agreement with data of reference [14].

Specific heat measurements were performed with an usual transient heat pulse technique [16], on a dilution refrigerator between 70 mK and 4 or 7 K, or a He³ cryostat between 4 and 40 K (in the case of AlCuFe12-(b)). For information, time constants of the exponential thermal transients are always larger than 10 s (up to 1000 s at 0.1 K) in the dilution set-up, and between 5 and 400 s (from 7 K to 40 K) in the He⁴ set-up. In the case of AlCuFe12-(b) and AlCuFe12.5, the convenient shape of the sample with two large flat surfaces of about 1.5 cm² yields an excellent thermal diffusivity in response to heat pulses and so very precise calorimetric data. Sample AlCuFe12-(b) was measured in two steps, firstly the whole sample in the dilution cryostat between 65 mK and 7 K, secondly a part of this sample (1.334 g mass) in the He⁴ cryostat between 7 and 40 K.
Fig. 1. — Specific heat data $C/T$ versus $T^2$ of Al$_{63}$Cu$_{25}$Fe$_{12}$-(a) obtained from two different experiments: symbol (o) and continuous line represent the data and fitting procedure from Klein et al. [10], symbol (●) for our present data and reference [11]. The dashed line represents the specific heat of Al$_{63}$Cu$_{25}$Fe$_{12}$-(b) for comparison (see Fig. 2).

3. Specific Heat Results and Analysis

A large part of the data discussed here were presented in two short reports in [11,17], with a preliminary discussion. In a first step, we intend to analyze our data in the usual way, as done by all other groups in previous publications [10,18–20], in order to extract the electronic and lattice contribution. For this purpose, data are reported in Figures 1 to 4 in the conventional plot $C/T$ versus $T^2$, in order to check temperature dependences in the form:

$$C_p = \gamma T + \beta T^3$$

with $\gamma$ the electronic Sommerfeld coefficient, and $\beta T^3$ the Debye acoustic limit, from which one can extract the Debye temperature $\theta_D$. Indeed, the cubic regime for the lattice contribution in crystalline solids is generally obeyed for $T \leq \frac{2}{3} \theta_D$ and then extends in the case of metals or (semi-) metallic alloys at least up to $T \sim 4$ K [21]. At higher temperature, deviations from the Debye regime are well accounted for by additional terms as $\delta T^5 + \cdots$ which correspond to an increase of the vibrational density of states (DOS) more rapid than $\omega^2$, as $g(\omega) = a\omega^2 + b\omega^4 + \cdots$ [21]:

$$C_p = \gamma T + \beta T^3 + \delta T^5.$$

In Figure 1 are reported the data of AlCuFe$_{12}$-(a) and (b) in the $T$-range $\sim 0.3–7$ K. For sample (a), we have replotted on this larger scale the data of Klein et al., published in [10] and fitted by formula (2) used by these authors with $\gamma \simeq 0.3$ mJ/mol K$^2$ and $\beta = 0.039$ mJ/mol K$^4$ which corresponds to a Debye temperature of 370 K.

The second series of data for this sample (a), below 3.5 K, were obtained from our measurements and partially published in [11]. There is a quite good agreement in the range of overlap of the two experiments. But we estimate that the data of reference [10] (symbols ○) are not
sufficiently accurate, nor the density of data large enough in the low \( T \)-range (\( T < 4 \) K) to conclude that expression (2) is still valid using the same values of \( \gamma \) and \( \beta \) as determined in the whole \( T \)-range of fitting, i.e. between 1.5 and 12 K. Indeed our data of better precision and extended at lower temperature (see also Fig. 3), clearly show a continuous flattening-off in \( C/T \) for \( T \rightarrow 0 \), and even a slight upturn at \( T < 1.2 \) K, in contradiction with the expression (2). A similar behaviour occurs in the high precision data (better than in the case of AlCuFe\(_{12.5}\)-(a)) obtained for AlCuFe\(_{12.5}\)-(b) and AlCuFe\(_{12.5}\) which are reported successively in the intermediate (0.1 \( \leq T^2 \leq 50 \) K\(^2\)) and low (0.1 \( < T^2 \leq 12 \) K\(^2\)) \( T \)-range in Figures 2 and 3, respectively. In the case of AlCuFe\(_{12.5}\)-(b), \( C/T \) saturation occurs progressively towards a constant slope for \( T \rightarrow 0 \), and it is possible to fit data by expression (1) within the experimental uncertainty only for \( T^2 < 4 \) (dashed line in Fig. 3), which yields \( \gamma = 0.345 \) mJ/mol K\(^2\) and \( \beta = 0.011 \) mJ/mol K\(^4\) corresponding to \( \theta_D = 560 \) K. So that we can wonder whether a \( T^3 \) regime really exists over a significant \( T \) interval: in fact, below 1 K the weight of the \( \beta T^3 \) term becomes rapidly negligible compared to that of \( \gamma T \), and so to total \( C_p \) (3% at 1 K). Between 1 and 2 K, the contribution of \( \beta T^3 \) remains below 10% of total \( C_p \) (this proportion is almost similar for AlCuFe\(_{12.5}\)). We will establish later that a more probable law for the lattice contribution between 1 and 10 K is \( \beta' T^{3.87} \): between 1 and 2 K there is only 1.5% of difference on the total \( C_p \) if one uses for the lattice term either \( \beta T^3 \) or \( \beta' T^{3.87} \) variations, which is of the order of uncertainty of the data.

As in the case of AlCuFe\(_{12.5}\)-(a), an upturn develops in \( C/T \) for AlCuFe\(_{12.5}\) below 1 K, that will be discussed more precisely with the data below 1 K (Fig. 8, and formula (4)). In those cases, we did not try to extract any \( \theta_D \) value.

Fig. 2. — Specific heat data of i-Al\(_{63}\)Cu\(_{25}\)Fe\(_{12}\)-(b) and i-Al\(_{62}\)Cu\(_{25.5}\)Fe\(_{12.5}\) for 0.3 \( \leq T \leq 7 \) K. The dashed-dotted line for AlCuFe\(_{12.5}\)-(b) shows the acoustic limit obtained from Brillouin spectroscopy (\( \beta = 0.0143 \) mJ/mol K\(^3\)). Continuous lines are only guides for the eye. In the inset, two limit fits to the data of AlCuFe\(_{12.5}\)-(b) are shown: the dashed straight line is a fit with \( \gamma T + \beta T^3 \) (\( \gamma = 0.345 \) mJ/mol K\(^2\) and \( \beta = 0.011 \) mJ/mol K\(^4\)) which is valid only for \( T^2 \leq 4 \) (K\(^2\)), and the continuous line, with the additional \( \delta T^5 \) term (\( \delta = 6.35 \times 10^{-4} \) mJ/mol K\(^5\)), valid up to \( T^2 = 20 \) (K\(^2\)).
We account for the differences of $C_p$ between the two samples AlCuFe$_{12}$-(a) and (b) probably to differences in exact compositions (we have previously noted that differences up to 0.5 at.\% Fe or Cu can occur between the two samples), or structural icosahedral quality, as discussed in Section 2. Similar variations are reported by Pierce et al. [19] among Al-Cu-Fe samples with slight compositional differences: 1 or 2 at.\% in Fe and Cu.

Similar deviations from relation (1) were systematically observed for precise data obtained in this low $T$-range ($1 \leq T \leq 3-4.2$ K) by the group of S.J. Poon in different species of icosahedral alloys, all being characterized by quite high Debye temperatures: i-AlCuRu with $\theta_D$ around 500 K [18], i-AlCuRuSi with $\theta_D$ between 445 and 485 K [19], and finally in different icosahedral and one rhombohedral approximants (r-AlCuFe) of the AlCuFe system, with $\theta_D$ included between 540 and 560 K [19]. Exactly as in the present case of AlCuFe$_{12}$-(b), a curvature in the $C/T$ versus $T^2$ plot remains towards the low temperatures, so that the relation (1) can only hold between 1 and 1.7 K! The authors extracted the $\gamma$ and $\theta_D$ values from a fit by expression (2) over the $T$-range of measurements. In addition, for the composition i-Al$_{62.5}$Cu$_{24.5}$Fe$_{13}$, $C/T$ shows an upturn below 1.4 K rather similar to the case of present AlCuFe$_{12}$-(a) or AlCuFe$_{12.5}$.

On the other hand, Wang et al. [20] have measured between 1 and 2.8 K two samples of Al$_{62}$Cu$_{25.5}$Fe$_{12.5}$ which differ by their structural state, one "phason-strained" and the second "phason-free", which is assumed to have recovered the perfect stable icosahedral state. In both cases relation (1) is well obeyed, which yields $\theta_D$ values much smaller than in the previous cases: 273 and 350 K for the phason-strained and the phason-free samples, respectively. But in our opinion, the analysis is based on a too narrow temperature interval.

All these data and the values of $\gamma$ and $\theta_D$ resulting from the fit to data by relations (1, 2) are collected in Table I.
within the usual frame of a cubic lattice contribution, it is interesting to compare the $\theta_D$ value obtained from calorimetric experiments to that extracted from acoustic data: sound velocities directly measured by Brillouin spectroscopy [22] or deduced from the acoustic dispersion relations by inelastic neutron scattering [23, 24]. From the mass density ($\rho = 4.4 \pm 0.1$ g/cm$^3$ measured for our both samples) and a mean Debye sound velocity $v_D$ (defined as $3v_D^3 = 2v_i^3 + v_f^3$) of $4.26 \times 10^3$ m/s from Brillouin experiments and $3.88 \times 10^3$ m/s from neutron experiments one can deduce elastic $\theta_D = 514$ K and $468$ K from Brillouin and neutron experiments, respectively (the corresponding $\beta_ac T^3$ terms, with $\beta_ac = 1944(1/\theta_D)^3$ J/mol K$^4$, are 0.0143 mJ/mol K$^4$ and 0.0190 mJ/mol K$^4$, respectively). We recover a rather good numerical agreement for our data below $\approx 2.5$ K with the elastic limit deduced from the Brillouin experiments, as we can verify in Figures 2 and 3. We note at this step that data from Wang et al. [20] are in large excess to this limit. This is understandable for their “phason-strained” sample, but not for the “phason-free” sample, which is considered to have recovered the perfect icosahedral structure after subsequent thermal treatment.

Such deviations from the Debye law are rather unexpected at so low temperatures (around 2 K) compared to the high $\theta_D$ values, as $\theta_D/50$ is around 10 K. We can refer here to the case of the semiconducting alloy Al$_2$Ru which was investigated by Pierce et al. [25] to draw comparison with the transport properties of i-AlCuRu and i-AlCuFe. Not only the electrical conductivity, but also low-T specific heat show very different behaviour from the QC’s: it is remarkable that although $\gamma$ and $\beta$ values are similar to those of QC’s ($\gamma = 0.13$ mJ/mol K$^2$, $\beta = 0.011$ mJ/mol K$^4$, $\theta_D = 570$ K; the reported $\delta T^5$ correction, with $\delta = -2 \times 10^{-6}$ mJ/mol K$^6$, is totally negligible in this $T$-range), the lattice contribution obeys the cubic law at least up to 8 K.
Also unexpected is that an attempt to fit our data of AlCuFe\textsubscript{12}-(b) by expression (2), which works well between 1 and 4.5 K (see the inset of Fig. 2) as in the case of reference [19] in the same T\textsuperscript{2} regime, fails for $T^2 \geq 20$ (K\textsuperscript{2}): surprisingly, $C_p$ increases less rapidly than predicted by formula (2). This is also in sharp contrast with the general behaviour of crystalline compounds where additional terms as $(T^5 + T^7)$ can account for deviations from the $T^3$ limit regime.

We have extended the data at higher temperature, from 7 to 40 K, using a second experimental set-up, on a part of the initial sample AlCuFe\textsubscript{12}-(b). As one can see in Figure 4, the overlap of data between the two experiments is very good. In this figure, we verify that the progressive deviation from a limit $T^3$ regime develops continuously up to 10 K. This is clearly seen in Figure 5 where the contribution of the lattice specific heat $C_l$, after subtracting the electronic contribution from total $C_p$, is plotted as $C_l/T^3$. This diagram is more sensitive than $C/T$ versus $T^2$ to study deviations from the Debye regime.

Two features appear in this diagram:

a) a broad bump develops, with its maximum located at $T = 23$ K; in the whole T-range, $C_l$ considerably exceeds the low T-regime;

b) no $T^3$ regime appears down to 1 K, i.e. in the temperature range where the contribution of the lattice to the total $C_p$ is not negligible (it remains larger than 3% of $C_p$).

The second property is supported by the plot log $C_l$ versus log $T$ reported in Figure 6 (see also in Fig. 7 the $T$-range 1–10 K), which shows that actually $C_l$ obeys a power law with the exponent 3.87, with an accuracy better than 10% between 1.2 and 12 K, that is over one decade of temperature.

As previously pointed out, the uncertainty on $C_l$ increases very rapidly below 1 K and consequently it is not possible to determine the exact $T$ dependence of $C_l$ below $\sim 1.2$ K: either $T^3$ or $T^{3.9}$. We outline that the best fit to the data in the $T$ range 1–10 K is given by a unique power law; any attempt to fit by expression (2) by varying $\beta$ or $\delta$, yields larger distortions in comparison with the experiment. As seen in Figure 5, $C_l$ leaves the power-law regime around 10 K, before reaching the maximum in $C/T^3$ at $T = 23$ K.
Fig. 5. — The lattice specific heat $C_l$ of $Al_{63}Cu_{25}Fe_{12}$-(b), obtained after subtracting from $C$ the electronic contribution $\gamma T$ ($\gamma = 0.345 \text{ mJ/mol K}^2$), divided by $T^3$. The two different symbols correspond to data obtained with two different experimental set-up. The two horizontal dashed lines represent cubic regimes corresponding to the acoustic limit ($\beta_{ac} = 0.0143 \text{ mJ/mol K}^4$) and to the possible fit for $T \leq 2 \text{ K}$ in a $C/T$ versus $T^2$ diagram (see Fig. 3) with $\beta = 0.011 \text{ mJ/mol K}^4$. The dashed dotted line represents the power law $T^{3.87}$ obeyed between $\sim 1$ and $10 \text{ K}$, as shown in Figures 6 and 7.

Fig. 6. — The lattice specific heat $C_l$ of $Al_{63}Cu_{25}Fe_{12}$-(b), defined as in Figure 5, but directly reported in a log-log plot between 0.3 and 40 K. The fit represents the power law $C_l = 0.006 T^{3.87} \text{ (mJ/mol K)}$.

Finally the specific heat of $AlCuFe_{12}$-(b) can be described with an accuracy better than 10% in the $T$ interval $\sim 0.1$ to $10 \text{ K}$ by:

$$C_p = \gamma T + BT^{3.87}$$  \hspace{1cm} (3)

with $\gamma = 0.345 \text{ mJ/mol K}^2$ and $B = 0.006 \text{ mJ/mol K}^{4.87}$

Now we consider the case of $AlCuFe_{12.5}$. The analysis seems to be more difficult than previously as there is no strict linear variation, particularly at low $T$, where there occurs an upturn in the usual $C/T$ versus $T^2$ diagram (see Fig. 3), except in a short interval ($1.5 \leq T^2 \leq 5$)
Fig. 7. — The lattice specific heat of Al₆₃Cu₂₅Fe₁₂-(b) and Al₆₂Cu₂₅.₅Fe₁₂.₅ in a log-log plot, between 1 and 10 K. The lattice contribution is obtained after subtracting from $C$ the “electronic” contribution determined in the low-temperature range ($T \lesssim 1$ K: see Fig. 8). The fits represent the power laws $T^{3.87}$ and $T^{3.55}$ obeyed by AlCuFe₁₂-(b) and AlCuFe₁₂.₅, respectively.

where the slope of the curve agrees numerically with the acoustic cubic law (this slope is indicated by the dashed-dotted line through the data of AlCuFe₁₂-(b)). Again, one can wonder about the validity of the cubic regime obeyed over so a narrow $T$-interval. However data below 1 K are of much more help: instead of a strictly linear variation, $C_p$ obeys a power law with a slightly sub-linear exponent, exactly as $T^{0.88}$, very similar to AlCuFe-(a) (see below Fig. 8). As in the previous case, due to the similarity of magnitude of $C_p$ in all samples, the influence of the acoustic term which remains close to the numerical values of $\beta_{ac}T^3$, vanishes rapidly below 1 K, so that the determination of this “electronic” contribution is very precise. In a similar way as for AlCuFe₁₂-(a) if one extrapolates above 1 K this $T$-dependence, the total specific heat of AlCuFe₁₂.₅ obeys with an accuracy better than 10%, in the $T$ interval ~ 0.1 to 7.₅ K, the law:

$$C_p = AT^{0.88} + BT^{3.55}$$  \hspace{1cm} (4)

with $A = 0.41$ mJ/mol $T^{1.88}$ and $B = 0.014$ mJ/mol $T^{4.55}$ representing the numerical coefficients of the “electronic” and lattice terms, respectively. The power law $T^{3.55}$ variation for the lattice term of AlCuFe₁₂.₅ is shown in Figure 7, together with the $T^{3.87}$ regime for AlCuFe₁₂-(b).

Analysis in the Temperature Range Below 1 K. — In Figures 8 and 9, specific heat data of the three samples are reported in a direct log-log plot in the $T$-range from 70 mK to 2 K. Let us outline the very good accuracy of data in this range (a scattering of a few percent), due to the good thermal diffusivity of samples together with the very small contribution of addenda, generally less than 10% of the total heat capacity. This allows us to determine the coefficient of the power law obeyed below 1 K over about one decade of temperature with a precision of ~ 1%. The results are the following:

(i) For AlCuFe₁₂-(b), $C_p$ reaches smoothly a strictly linear $\gamma T$ variation ($\gamma = 0.345$ mJ/mol K²): the deviation from the linearity is only 1% at 1 K, which confirms that the lattice contribution analyzed as $\beta T^3$ with $\beta = 0.011$ mJ/mol K⁴, is overestimated. Below 0.15 K a slight deviation
Fig. 8. — Specific heat between 70 mK and 2 K of the same samples as in Figure 3 (same symbols) in a log-log plot. Below 0.2 K, a slight nuclear contribution has been subtracted for Al$_{62}$Cu$_{25.5}$Fe$_{12.5}$ (see Fig. 9) and Al$_{63}$Cu$_{25}$Fe$_{12}$-(b), represented by the dashed line for this latter sample. Straight lines indicate power law $T^\nu$ variations, with $\nu$ close to 0.9 in the case of AlCuFe$_{12.5}$ and AlCuFe$_{12}$-(a), and exactly 1.0 for AlCuFe$_{12}$-(b).

from $\gamma T$ occurs (dashed line in the figure), so that $C_p$ can be analyzed down to 65 mK as:

$$C_p = C_N T^{-2} + \gamma T,$$

sum of an hyperfine nuclear term, likely of magnetic origin, with $C_N = 2.1 \times 10^{-5}$ mJ K/mole, and the electronic term. Hence, after subtraction of the (extrinsic) nuclear term, the linear variation $\gamma T$ is defined within less than 2% between 65 mK and 1 K.

(ii) For AlCuFe$_{12}$-(a), $C_p$ obeys the sub-linear power law $AT^{0.90}$ between 0.1 and 1.5 K ($A = 0.44$ mJ/mol K$^{1.9}$), without any deviation at low temperature. There is no detectable contribution of a nuclear term.

(iii) On the contrary, in the case of AlCuFe$_{12.5}$ a rather large nuclear contribution develops below 0.2 K. Between 70 mK and 1 K, $C_p$ is well analyzed as:

$$C_p = C_N T^{-2} + AT^{0.88},$$

with $C_N = 2.15 \times 10^{-4}$ mJ K/mole and $A = 0.41$ mJ/mol K$^{1.88}$. We observe that the departure from the power law above 1 K is more rapid than in the case of AlCuFe$_{12}$-(b) since the vibrational lattice contribution is two times larger.

The hyperfine nuclear term is here ten times larger than in AlCuFe$_{12}$-(b), and it seems completely absent in AlCuFe$_{12}$-(a), so we conclude to a magnetic extrinsic origin. Although
the magnetic investigations did not reveal much difference between the three samples, it can be related to a minute amount of crystalline second phase, as the presence of such $\beta$-phase has been detected in AlCuFe$_{12.5}$, or to some iron clusters which develop upon annealing from the icosahedral phase (Ref. [12]). We note that the maximum amplitude of this term ($C_N = 2 \times 10^{-7}$ J K/mole) remains very low in comparison to the series i-AlPdMn or i-ALMn where its origin is there related to the magnetism of a few percent of Mn atoms, frozen in a spin-glass state [3].

On the other hand, it is not possible to ascribe the sub-linear regime of $C_p$ to a possible magnetic (electronic spins) contribution, as previously suggested by Pierce et al. at the origin of the upturn of $C/T$ in AlCuFe [19]. This temperature dependence is too smooth to be interpreted by a Schottky anomaly, or by a spin-glass transition as in i-ALMn or AlPdMn [3,26]. In addition, the $T^{0.90}$ variation is observed on a sample which has been proved to remain diamagnetic down to low temperatures as 4 K [9], with the minimum content of magnetic moments.

At this step, we can consider two possibilities for the sub-linear regime: either an electronic origin due to the localization of a part of electrons or to configurational excitations, typically tunnelling “Two-Level States”. Both will be discussed shortly in Section 4.2.
4. Discussion

4.1. Vibrational Excitations. — Firstly, we briefly comment on the results of conventional specific heat analysis based on formulas (1, 2), from which are extracted the Debye temperature and the electronic coefficient $\gamma$ related to the DOS at the Fermi level. We restrict to the results of analysis of data in the $T$-range 1–3 K for reliability of the conclusions (see Tab. 1). One main result is probably that, whereas $\theta_D$ can be very sensitive to the conditions of preparation, as particularly evidenced by the experiments of Wang et al. [20], $\gamma$ remains almost insensitive: for all i-phases, the $\gamma$ value remains included between 0.30 and 0.35 mJ/mol K$^2$, whereas $\theta_D$ can change by a factor of two, which means about 10 for the lattice specific heat. There is a good agreement between the $\theta_D$ value of the present AlCuFe$_{12}$-(b) which is in the form of large size polycrystalline sample and those of Al$_{62.5}$Cu$_{26.5}$Fe$_{11}$ (i-phase and rhombohedral approximant) and i-Al$_{63.5}$Cu$_{24.5}$Fe$_{12}$ from Pierce et al. [19] which were obtained by melt-spinning in the form of ribbons of $\sim$ 20 $\mu$m thickness. Although these three i-phases correspond to the metastable i-composition, their high Debye temperatures are a strong indication for the structural quality and absence of parasitic phases. There is also an excellent agreement between the $\gamma$ values of these three samples, which, as it is well-known, represent about 1/3 of the free-electron value. We can also conclude to the relative good agreement, despite the uncertainty in the determination of $\theta_D$ from specific heat, between the calorimetric and acoustic values of $\theta_D$.

Now, we intend to compare our data to other experimental results on the vibrational properties of QC’s, principally obtained by inelastic neutron scattering techniques, either on single-grained samples for the determination of the phonon dispersion relations, or on large polydomain samples by time-of-flight (TOF) experiments for the determination of the generalized vibrational density of states (GVDOS) up to a large energy of around 50 meV.

In comparison to conventional crystalline materials, the phonon dispersion relations $\omega(q)$ are very unusual in QC’s, and show several common features among the different species: AlLiCu [27,28], AlCuFe [23,24] and AlPdMn [29,30]. Well defined propagating phonon modes with isotropic sound velocities are measured by inelastic neutron scattering only in the vicinity of the strong Bragg peaks, for energy up to $\sim$ 3 THz or 12 meV. (1 THz = 4.13 meV). In the case of AlPdMn, for which exists the most complete study due to the quality and size of the single-grained samples, these acoustic modes become rapidly dispersionless at increasing q, for a corresponding energy of 3 THz (a strict separation between their acoustic or optic character was not clearly established in Ref. [29]). Simultaneously, they broaden considerably, with a width of about 1 THz [29]. In addition, a band of optic modes of various intensities, with a similar width of $\sim$ 1 THz, was detected between 1.8 and 5.5 THz [30]. The unusual broadening of the acoustic modes appears to be a direct consequence of the quasiperiodic structure, as a probable indication of their progressive localization with increasing frequency [31].

In the case of AlCuFe, acoustic modes corresponding to linear dispersion relations have been clearly identified by neutron experiments in a monodomain sample of Al$_{63}$Cu$_{25}$Fe$_{12}$ up to energy of 2.5 THz [23]. Subsequent measurements could follow this unique degenerate transverse acoustic (TA) branch up to 3.8 THz [24]; they also indicate the progressive bending of the dispersion curve and broadening of the phonon linewidth (up to $\sim$ 1 THz) at increasing $q$, as in AlPdMn. However, no optic mode could be detected in this energy range, perhaps due to the small size of the sample which does not allow sufficient resolution.

The generalized vibrational DOS (GVDOS) obtained by TOF inelastic neutron scattering can be compared to the characteristic frequencies determined in the phonon dispersion relations. In the case of AlPdMn [32,33], the first broad peak at 16 meV in the GVDOS is in agreement with the optic mode, measured in various positions of the reciprocal space at around 4 THz [29]. However, there is no relation between the DOS and optic modes at lower frequency, such
as 1.8 and 3 THz [30]. In the case of AlLiCu, the comparison between the two techniques gives some discrepancy (see discussion in Ref. [34]): the DOS shows a peak at 13 meV, whereas the dispersionless mode is located at 10 meV [27]. For Al_{82}Cu_{25.5}Fe_{12.5}, the first broad peak in the GVDOS occurs around 14 meV [35]. In addition, dispersion relations also extracted from neutron TOF show almost flat bands with some dispersion lying around 11-12 meV [36]. On the low-energy range, GVDOS cannot generally be determined below a few meV (8 meV in the case of AlPdMn), and so it is difficult to verify the validity of the $\omega^2$ acoustic regime from the TOF technique in the corresponding $T$-range ($T \lesssim 10$ K) of specific heat measurements.

Several theoretical models could well reproduce the main properties of the phonon dispersion relations (see Ref. [31] for AlPdMn) and of corresponding VDOS. Generally they predict a large number of broad dispersionless optic modes (or stationary modes) as the direct consequence of the hierarchical distribution of quasi-Brillouin zone boundaries. Starting from a three-dimensional structural model, Hafner et al. [34,37] could simulate the dispersion relation and the vibrational DOS of AlLiCu and AlMgZn QC’s: they have confirmed the existence of well-defined propagating phonons, up to energy of $\sim 8-10$ meV for the transverse modes, close to the most intense Bragg peaks, and established a hierarchy of stationary, dispersionless (optic-like) modes at higher energy, extending almost everywhere in the q-space, outside of the most intense reflections. In agreement with the experiments, they show the correlation between the peaks in the VDOS and the frequency of the stationary modes, with a first peak centered at 10 meV.

In comparison to these results, our calorimetric study shows:

(i) The presence of a broad maximum in $C/\rho T^3$ at $T \approx 23$ K which indicates the presence of dominant modes at energy of 115 K or 10 meV (or 2.4 THz) in the vibrational DOS [38]. This energy is characteristic of intense optic-like (or dispersionless TA) modes in AlLiCu, AlPdMn, AlMgZn QC’s. Such modes have not still been detected in AlCuFe. The GVDOS shows a first broad peak at somewhat higher energy ($\sim 14$ meV). However discrepancies of this order have been detected in AlLiCu: the dispersionless branch lies at 10 meV compared to the first peak in GVDOS at 13 meV.

(ii) A deviation of $C_p$ from the acoustic cubic regime at temperatures as low as $T = 2$ K, and even no clear evidence for the existence of this regime down to 1 K. In contrast, the vibrational specific heat is well analyzed in an extended $T$-range from 1 K to 7 or 10 K with the power laws $T^{3.6}$ and $T^{3.9}$ for AlCuFe$_{12.8}$ and AlCuFe$_{12.8}$(b), respectively. That means that the vibrational DOS deviates from the $\omega^2$ regime expected for purely acoustic modes, corresponding to linear dispersion relations, not only around the energy of the dominant peak at 10 meV, but down to very low energies of the order of 0.5 meV. Such a deviation cannot be accounted for by the broadening of the phonon acoustic lines which starts at energy of about 2 THz ($\sim 8$ meV), when the dispersion relations begin to deviate from linearity [24,29].

We rather propose that this “excess” DOS could originate from optic-like modes extending down to very low energies. Indeed, contrary to the propagative-acoustic modes well located near the few most intense Bragg reflections, the optic-like, stationary modes lie everywhere in the q-space: by neutron spectroscopy, they are detected close to every Bragg peak, whatever its intensity is [30]. Consequently, due to high density of diffraction peaks intrinsic to the quasiperiodic structure, they act as the dominant vibrational excitations even at low frequencies. As they are characterized by an important broadening which extents down to energy of $\sim 1$ THz (see Figs. 3, 4 in Ref. [30]), they cover an energy range of the order of whole the vibrational spectrum between $\sim 1$ and 8 THz [39]. One can conjecture that their contribution to the VDOS, in addition to that of propagative phonons, extend down to less than 1 THz, as suggested from the scattering in energy of neutron data. Within this hypothesis, the deviation of $C_p$ from the acoustic Debye limit which starts at $\approx 2$ K would imply an extension in
energy down to \( \approx 0.2 \) THz. The power law \( T \)-dependence of \( C_p \) could be a consequence of the hierarchical distribution of the stationary modes [34] (1).

Finally these very unusual vibrational properties are at the origin of a lattice thermal conductivity behaviour which is somehow reminiscent of the amorphous materials, as the small amplitude and a characteristic plateau starting at \( \sim 10 \) K (see a discussion of recent data in Ref. [39]).

4.2. Electronic Excitations. — We consider now the low \( T \)-range below 1 K where the deviations from the \( \gamma T \) variation expected for a classical electronic contribution have been established. Two different origins can be considered, and none can be ruled out on the basis of available experimental informations.

The first possibility is a purely electronic origin, within the hypothesis of the proximity of a metal-insulator transition as already proposed for this system [11,40], by analogy with experimental results in crystalline doped semiconductors [41]. In that case, when approaching the transition from the metallic side, a specific heat contribution due to the localized electrons \( \Delta C \sim T^\alpha \) (with \( \alpha < 1 \)) occurs below 1 K in addition to the regular \( \gamma T \) contribution of the itinerant electrons, so that the total electronic specific heat \( C_e = \gamma T + \Delta C \) can be approximated by a sublinear power law. The main difficulty in our case is the exact determination of \( \gamma \), which is not possible from a \( C/T \) versus \( T^2 \) diagram, contrary to the case of crystalline semiconductors [42]. We have tentatively done such an analysis for AlCuFe\(_{12-}\)(a): with the hypothesis of a plausible \( \gamma \) value of 0.30 mJ/mol K\(^2\), as shown in Figure 10, it yields for the localized electronic contribution a variation \( \Delta C \sim T^{0.73} \). A similar quantitative analysis can be obtained for AlCuFe\(_{12.5}\).

To verify this hypothesis, we have to check the trend of conductivity between the different samples. In agreement with previous studies [14], there is evolution towards a more insulating state from Al\(_{63}\)Cu\(_{23}\)Fe\(_{12}\) towards Al\(_{42}\)Cu\(_{35.5}\)Fe\(_{12.5}\) and this latter composition has been considered as a critical one, for which the AlCuFe samples are the closest to the metal-insulator transition [40]. Simultaneously, we observe the occurrence of the sublinear \( T^0.7 \) contribution for AlCuFe\(_{12.5}\), in comparison to AlCuFe\(_{12-}\)(b), two samples of similar icosahedral structural quality. However, the same sublinear term is present in AlCuFe\(_{12-}\)(a), which presents a resistivity very close to that of sample-b (\( \rho_{300K} \) is only 5% lower in sample (a) compared to (b)).

The second possibility is a contribution from low-energy configurational excitations of the type of tunneling two-level states (TLS) in amorphous materials, the existence of which has been proved in the QC's as early as in 1987 in the metastable AlMgZn or in the imperfect stable AlLiCu [43]. More recently, they were confirmed to be also present in the perfect, stable AlPdMn phase, either by acoustic [44] or thermal conductivity [45,46] measurements. But at variance to amorphous systems, their concentration appears to be sample dependent [46], even in the case of perfect icosahedral quality. This origin could explain in the present case the variation of the power-law regime among the three samples, with a minimum contribution for AlCuFe\(_{12-}\)(b): from X-ray characterization, it appears that this ingot is of best structural quality, from the sharpness of the diffraction lines and the complete absence of trace of second phase. This is also supported by the overall lower vibrational contribution to \( C_p \) above 1 K.

In order to give a numerical estimation of the TLS contribution, we have to subtract from total \( C_p \) the electronic contribution: this is a similar analysis as in the previous one for of the localized electronic contribution. However, even in the case of a strictly linear variation of \( C_p \) one

(1) Note added in proof: During the submission of this paper, a publication from C. Janot (J. Phys. Condens. Matter 9 (1997) 1493) appeared where the author proposed a structural model based on a hierarchy of clusters, which yields a variation of the lattice specific heat as \( T^{n+1} \), with \( n \) slightly larger than 2.
cannot exclude a linear contribution from the TLS's: in such a case the numerical estimation is impossible. In the case of the sublinear variations of $C_p$ (for AlCuFe$_{12}$(a) and AlCuFe$_{12.5}$), and with the same hypothesis of an itinerant electronic contribution $\gamma \simeq 0.30-0.35 \text{ mJ/mol K}^2$, this yields a residual contribution:

$$\Delta C \simeq 0.14 \, T^{0.73} \text{ to } 0.10 \, T^{0.68} \text{ (mJ/mol K)}, \quad \text{or} \quad 35 \, T^{0.73} \text{ to } 25 \, T^{0.68} \text{ (erg/g K)}.$$ 

These numerical values can be compared to those of amorphous metallic alloys [47,48], where TLS excitations can also be at the origin of sublinear ($\sim T^{0.5}$) contributions, with an amplitude of a few erg/g K at $T = 0.1$ K [48]. Here $\Delta C$ reaches $\simeq 5$ erg/g K at $T = 0.1$ K, which corresponds to the upper range in amorphous alloys.

5. Conclusion

From this calorimetric study performed on a quite broad temperature interval, we have pointed out that the lattice specific heat deviates from the Debye regime at unexpected low temperatures. This property can be interpreted by the presence at low frequency of vibrational excitations rapidly in excess to the usual phonons, in agreement with the results of inelastic neutron scattering experiments which clearly distinguish the two types of excitations: well defined propagating phonon modes versus stationary, dispersionless vibrational modes. Such an unusual vibrational spectrum necessarily induces specific thermal properties, as here for the lattice heat capacity, and also for the related lattice thermal conductivity $\kappa$, which is much more similar to that of amorphous solids than of periodic crystals, with a very short phonon mean free for frequency of a few THz, at the origin of an extended plateau (or slight minimum) in $\kappa$. 

**Fig. 10.** — A tentative analysis of the sublinear ($T^{0.90}$) specific heat of Al$_{63}$Cu$_{25}$Fe$_{12}$(a) below 1.5 K: after subtraction of a free-electron contribution $\gamma T$ (with $\gamma \simeq 0.3 \text{ mJ/mol K}^2$), there remains a contribution $\Delta C \sim T^{0.7}$, the origin of which is discussed in the text. 

![Diagram showing specific heat analysis](image-url)
Another specific feature of the QC's, which is probably more sensitive to the structural quality of the samples than the vibrational excitations spectrum, is the TLS-like low-energy excitations which play a dominant role in the thermal properties below 1 K. Such an origin can explain the sublinear variations of the low-T specific heat that we have measured for some of the samples.

Acknowledgments

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References

[38] An Einstein oscillator at frequency $\omega_0$ induces a maximum contribution in $C/T^3$ at $T_m = \frac{5k\omega_0}{k_B}$.