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M. Bessière, A. Quivy, S. Lefebvre, J. Devaud-Rzepski, Y. Calvayrac. Thermal stability of Al-Cu-Fe icosahedral alloys. *Journal de Physique I*, 1991, 1 (12), pp.1823-1836. 10.1051/jp1:1991242 . jpa-00246453

**HAL Id: jpa-00246453**

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Submitted on 4 Feb 2008

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Classification

Physics Abstracts

61.10F — 81.30 — 81.40

## Thermal stability of Al-Cu-Fe icosahedral alloys

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(Received 11 April 1991, revised 19 July 1991, accepted 19 August 1991)

**Résumé.** — Une phase stable idéalement quasipériodique existe dans un petit domaine de concentration, au voisinage de la composition  $\text{Al}_{62}\text{Cu}_{25,5}\text{Fe}_{12,5}$ . La diminution de la teneur en fer, ou le remplacement de faibles quantités de cuivre par de l'aluminium, conduisent à des alliages icosaédriques qui subissent vers 650 °C des transformations structurales dont la nature n'est pas clairement identifiée : dans le diagramme de diffraction des rayons X sur poudre, les profils de raies deviennent purement Lorentziens ( $\text{Al}_{62,3}\text{Cu}_{25,3}\text{Fe}_{12,4}$ ) ou bien des raies diffuses apparaissent dans le pied des pics de Bragg ( $\text{Al}_{63}\text{Cu}_{24,5}\text{Fe}_{12,5}$ ). Dans ce dernier cas un long traitement de recuit transforme finalement les pics de Bragg en des pics diffus localisés à des positions clairement en dehors de celles correspondant à la symétrie icosaédrique idéale. De faibles écarts à ce domaine de compositions conduisent à des diagrammes de rayons X où les pics de Bragg sont épaulés quel que soit le traitement thermique ; l'ordre icosaédrique parfait n'est jamais obtenu pour ces compositions ( $\text{Al}_{63,25}\text{Cu}_{24,5}\text{Fe}_{12,25}$ ,  $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ ,  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ ).

**Abstract.** — A stable ideally quasiperiodic phase exists in a small range of concentration, close to the composition  $\text{Al}_{62}\text{Cu}_{25,5}\text{Fe}_{12,5}$ . Reducing the iron content, or replacing small amounts of copper by aluminium, lead to icosahedral alloys which exhibit around 650 °C structural transformations of unclear nature : in the X-ray powder diffraction pattern, the peak profiles become purely Lorentzian ( $\text{Al}_{62,3}\text{Cu}_{25,3}\text{Fe}_{12,4}$ ) or diffuse « side-bands » appear in the tails of the Bragg peaks ( $\text{Al}_{63}\text{Cu}_{24,5}\text{Fe}_{12,5}$ ). In the last case long annealing treatments eventually transform the Bragg peaks into diffuse peaks located at positions clearly off the ideal icosahedral symmetry. Small deviations from this composition range lead to Bragg peaks with shoulders whatever the heat-treatment may be ; perfect icosahedral order is never obtained for these compositions ( $\text{Al}_{63,25}\text{Cu}_{24,5}\text{Fe}_{12,25}$ ,  $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ ,  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ ).

### 1. Introduction.

The basic problem of describing the structure of the icosahedral phase is still controversial. Currently three kinds of models remain [1] : the ideal quasiperiodic model, the random tiling model, and the icosahedral glass model. The first model predicts sharp Bragg peaks with no diffuse intensity. The second model predicts sharp Bragg peaks plus additional diffuse intensity mostly located in the wings of the peaks. Finally the icosahedral glass model predicts

diffuse intensity all over the reciprocal space but strongly enhanced around the peak positions of the previous models.

Recent observations of scattering spectra in i-AlCuFe [2], i-AlCuRu [3] or i-AlPdMn [4] essentially validate the first two models. The main physical difference between these two models is the relative importance of energy *versus* entropy in the stabilization process of the icosahedral phase. The ideal quasiperiodic model asserts that the icosahedral phase is a ground state (at 0 K) of the phase diagram, i.e. that it corresponds to a minimum configurational energy. In the random tiling model the stabilization of the icosahedral phase is assumed to be due to the entropy term where the quasicrystalline state is selected by having a larger configurational entropy than the competitive crystal phases. The ground state can then be a periodic crystal. The question of the thermal stability of the icosahedral AlCuFe phase as a function of temperature is therefore of crucial importance to ascertain the validity of either of these two models.

The i-AlCuFe phase thermal stability and « perfection » (in the sense of diffraction peaks sharpness), after annealing at high temperature ( $> 800$  °C), are well established. However, several authors have described phase transformations when the samples are annealed between 600 and 750 °C. Goldman *et al.* [5] have shown that heat treatment of melt-spun  $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$  samples produces at 600 °C a clear broadening of X-ray diffraction peaks which exhibits a pronounced dependence on the magnitude of the phason momentum  $q_{\perp}$ . Bancel [6] has studied the temperature dependence of X-ray peak intensities on dodecahedral grains of the i-phase extracted from shrink cavities inside  $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$  ingots annealed for 10 days at 825 °C. Warming curves between 500 and 600 °C revealed a  $q_{\perp}$  dependent decrease of intensity. At 700 °C all peaks regain their lost intensity. Upon cooling the intensities are reversible down to 600 °C, and remain at their suppressed values. These data are explained by assuming a softening phason mode which drives a structural transformation, at 670 °C, to one or more low-symmetry phases. Audier *et al.* [7], studying dodecahedral  $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$  particles extracted from a slow cooled  $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  ingot, have observed a reversible structural transformation between a rhombohedral microcrystalline state at low temperature and a perfect quasicrystalline structure at high temperature *via* an intermediate modulated icosahedral phase which seems to occur between 650 and 750 °C. The transformations were studied *in situ*, by high resolution imaging and electron diffraction. The existence of a rhombohedral microcrystalline phase of overall pseudo-icosahedral symmetry has been confirmed by X-ray diffraction on dodecahedral particles extracted from the same ingot [8]. It might be concluded that Al-Cu-Fe quasicrystals are not stable below 650 °C, and transform to a crystalline state [7] or, at least, to an imperfect icosahedral state with large phason strains [5].

On the other hand, a previous preliminary study of the AlCuFe phase diagram [9] led us to conclude that a pure icosahedral phase does exist which does not exhibit any structural transformation in the full range of accessible temperatures. This apparent discrepancy in the literature is owed, to our point of view, to the crucial influence of the composition of the alloy on its structural properties. We present here the results of a systematic study of the thermal behavior of a set of icosahedral alloys in a narrow concentration window of the ternary phase diagram. All samples are « single-phased » in the sense that, after annealing at any temperature up to the solidus, there are no traces of any other phases of the equilibrium phase diagram as established by Bradley and Goldschmidt [10] (1).

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(1) The i-Al-Cu-Fe phase corresponds to the phase noted  $\Psi$  in the Bradley's phase diagram (see [9]).

## 2. Experimental.

The alloys were prepared from the pure elements (Al 99.99 %, Cu 99.95 %, Fe 99.95 %) by induction melting in an alumina boat under a controlled helium atmosphere. The whole ingots ( $\approx 5$  g) were remelted by induction heating in a silica tube and rapidly quenched by planar flow casting on a rotating copper wheel, under an atmosphere of pure helium.

Eleven different nominal compositions have been investigated (Fig. 1). Although the chosen compositions are very close to each other, the complexity of the diagram in that region is such that tiny changes in composition are sufficient to generate large differences in the thermal behavior of the alloys.

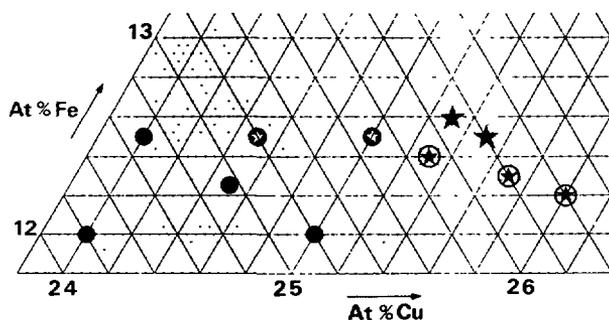


Fig. 1. — Thermal stability of the Al-Cu-Fe icosahedral phase as a function of composition : (★) Perfectly ordered i-phase from 800 °C to 400 °C. (⊙) Perfectly ordered i-phase at 800 °C ; change of profile of the X-ray peaks at 600 °C : the shape becomes Lorentzian. (⊗) Perfectly ordered i-phase at 800 °C ; peaks with shoulders at 650 °C. (●) The peaks always have shoulders whatever the heat-treatment up to the solidus. The intensity of the shoulders increases when temperature is lowered.

A major difficulty in mastering the alloy preparation is the existence of a peritectic transformation at high temperature. This induces a macrosegregation during the cooling process which finally leads to large compositional inhomogeneities in the master ingots slowly cooled from the liquid state. To reduce this intrinsic phenomenon, we found it efficient to prepare the samples by rapid quenching from the melt. Under these conditions, the fine solid grains formed from the liquid have uniform composition. The subsequent annealing treatments are performed at temperatures always below the solidus. The control of the final composition as compared to the nominal one remains a crucial difficulty. Standard chemical analyses are not sufficiently accurate to discriminate between such close compositions. We decided to assign the nominal composition to our alloys if, having prepared three different ingots of a given composition, we found the same thermal behavior in all three ingots. This insured that the systematic errors, if any, are comparable in all cases.

The flakes obtained by planar flow casting were ground and sifted through a 32  $\mu\text{m}$  sieve for powder X-ray diffraction measurements.

Most of the powder X-ray diffraction patterns were performed on a Philips diffractometer equipped with a curved graphite monochromator in the diffracted beam, using  $\text{CoK}\alpha$  radiation ( $\lambda = 1.7902 \text{ \AA}$ ). The instrument resolution, measured by the full width at half maximum (FWHM) of the (200) line from a standard  $\text{CeO}_2$  powder sample, was about  $0.08^\circ \theta$  :  $\Delta q \sim 1.5 \times 10^{-3} \text{ \AA}^{-1}$ , with  $q = (2/\lambda) \sin \theta$ .

High-resolution X-ray diffraction experiments were done using the synchrotron radiation on the line D-23 of LURE-DCI, which is equipped with a double-crystal monochromator

(Si 111) in the incident beam and an analyzer crystal (Ge 111) in the diffracted beam. At the wavelength chosen (1.7902 Å), the instrument resolution, measured by the FWHM of the (200) line of a standard CeO<sub>2</sub> powder sample, was about 0.02°  $\theta$  ( $\Delta q \sim 4 \times 10^{-4} \text{ \AA}^{-1}$ ).

The indexing of the diffraction patterns of the icosahedral phase has been performed in the scheme proposed by Cahn *et al.* [11].

### 3. Results.

**3.1 THE AS-QUENCHED STATE.** — The as-quenched state is two-phased : for all the alloys studied here (see Fig. 1 for compositions), the i-phase is accompanied by a small amount (volume fraction < 15 %) of a simple cubic FeAl-type phase (lattice parameter  $a = 2.92 \text{ \AA}$ ), which may be identified as the  $\beta_2$  phase in reference [10]. In the composition range studied the  $\beta$ -phase is stable only at high temperature, above 870 °C, and it is retained at low temperature by the quench. Its final proportion in the as-quenched samples depends on the cooling rate [12]. Electron micrographs show that the  $\beta$  particles are rejected to the interdendritic spaces (Fig. 2).

The as-quenched icosahedral phase presents an appreciable degree of disorder clearly observed in the X-ray diffraction spectra ; the deviations of the positions of the Bragg peaks from the calculated values and the intrinsic peak widths are similar to those previously



Fig. 2. — Transmission electron micrograph of an as-quenched Al<sub>62</sub>Cu<sub>255</sub>Fe<sub>125</sub> sample. The  $\beta$ -phase has been rejected to the interdendritic spaces.

obtained in  $i\text{-Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$  [9] and  $i\text{-Al}_{73}\text{Mn}_{21}\text{Si}_6$  [13]. The FWHM for all the lines of the X-ray diffraction spectrum obey a quadratic law as a function of the parallel ( $q_{\parallel}$ ) and perpendicular ( $q_{\perp}$ ) components of the 6D diffraction vector. This behavior is the same as that we have found for  $i\text{-AlMnSi}$ , and it is in agreement with a model of disorder due to frozen-in phason strains [14].

### 3.2 ANNEALED STATES.

**3.2.1 Elimination of the  $\beta$ -phase and the perfection of the  $i$ -phase.** — The  $\beta$ -phase initially present in the as-quenched samples is easily eliminated by annealing at low temperature: typical annealing for 1 h at 600 °C is sufficient to obtain single phased icosahedral samples. However the ultimate perfection of the  $i$ -phase is much more difficult to achieve. Preliminary results on the kinetics of elimination of the defects, as a function of temperature, show that at 600 or 700 °C the « perfect » quasiperiodic state is still not obtained even after annealing for 10 days. At 745 °C, for the  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$  alloy, the FWHM of the X-ray lines reduce to the instrumental width after annealing for 13 h.

As a rule, resolution-limited diffraction peak widths are obtained only by annealing a few degrees below the solidus temperature. At these temperatures, the time required for the defects to fully disappear is about one hour. After this treatment, the positions of the X-ray diffraction peaks are strictly those calculated for an ideal quasiperiodic phase: figure 3 shows that there is no shift in the peak positions, within the accuracy of the determination:  $|q_{\text{calculated}} - q_{\text{measured}}| < 5 \times 10^{-5} \text{ \AA}^{-1}$ . In this high-resolution experiment the order of magnitude of the error on the determination of the peak position:  $\Delta q = \pm 2 \times 10^{-5} \text{ \AA}^{-1}$ , corresponds to one step of the scan:  $0.002 \text{ } 2\theta$ . The 6D-lattice parameter,  $a_6 = 6.3179 \text{ \AA}$ , has been determined from the whole set of X-ray lines and the theoretical positions have been calculated using this value.

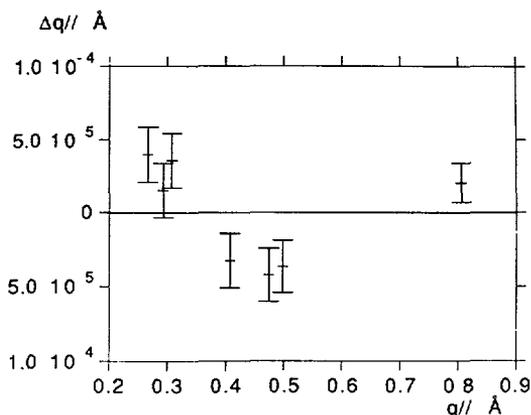


Fig. 3. — Deviations ( $\Delta q_{\parallel}$ ) of the measured peak positions from those calculated for an ideal quasicrystal (high-resolution experiment).

**3.2.2. Thermal stability as a function of concentration.** — We observed three different thermal behaviors in the studied composition range (Fig. 1). We give hereafter the results for some typical alloys:

i)  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$ . In this alloy the perfect  $i$ -phase, obtained by annealing the as-quenched samples between 800 and 820 °C, remains unchanged by further annealing at low temperatures.

This statement is justified by X-ray diffraction experiments and electron microscopy observations after long isothermal anneals at 600 °C (18 h) and at 500 °C (4 days), and after long cumulative heat-treatments from 600 to 400 °C.

Figure 4 gives the X-ray diffraction pattern after the following cumulative heat-treatments : 800 °C (2 h), cooling to 600 °C (3°/min), 600 °C (80 min), cooling to 575 °C (3°/min), 575 °C (65 h), slow cooling to 550 °C (5°/h), 550 °C (25 h), 520 °C (25 h), 470 °C (67 h) : there are no observable shifts in the peak positions, no broadening or change in profile of the peaks, even for large values of the perpendicular component of the 6D wave vectors (see for instance the (14,21) peak in Fig. 4). On the same sample, further anneals at 446 and at 400 °C for 5 days did not change the results. The same thermal behavior was observed for the  $\text{Al}_{62.1}\text{Cu}_{25.3}\text{Fe}_{12.6}$  alloy.

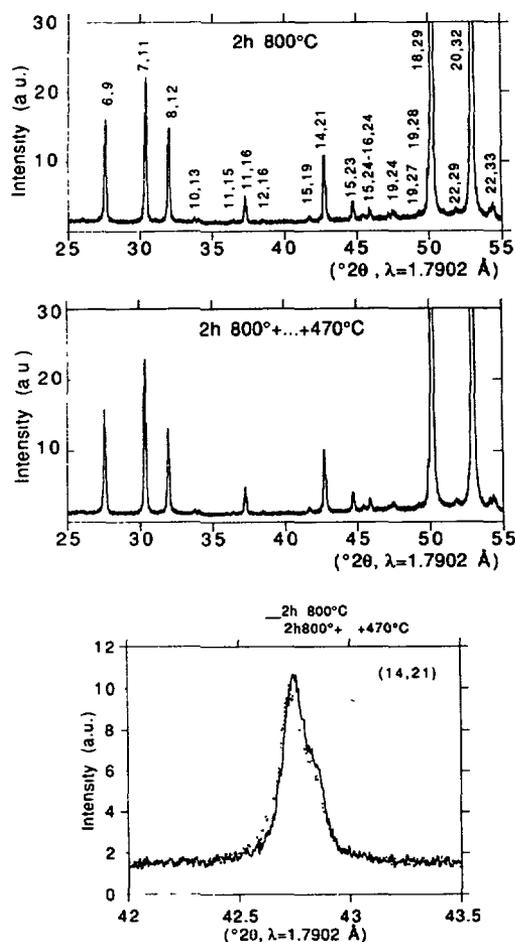


Fig. 4. — Thermal stability of the  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  i-phase. Sample annealed for 2 h at 800 °C, then successively annealed at 600, 575, 550, 520, 470 °C (see text) : no change in the diffraction pattern.

*These results, to our opinion, qualifies the icosahedral phase to be a possible ground state in this tiny region of the phase diagram.*

There is an apparent discrepancy between the present results and those obtained by Audier *et al.* [7], Dénoyer *et al.* [8] and Goldman *et al.* [5]. As recalled in introduction, these authors

claim that the Al-Cu-Fe i-phase, perfect at 800 °C, transforms at ~ 650 °C to a rhombohedral phase ( $a = 32.16 \text{ \AA}$ ,  $\alpha = 36^\circ$ ) [7-8], or — at least — to a more disordered phase [5]. It has to be emphasized that the perfect i-phase that we have just described is clearly different from the rhombohedral phase described in [8]. Looking at the diffraction pattern, in the small angles part, the two phases can be unambiguously distinguished. Figure 5 gives the relatively small angle part of the diffraction pattern, for the sample successively annealed at 600, 575, .., 470 °C. Comparing with the data given in [8], the following striking differences can be noted :

— the (2, 1) and (3,  $\bar{1}$ ) lines of the i-phase clearly appear in the present results ; they are not detected in [8] ;

— the (100), (110), (200), (220) lines of the rhombohedral phase, observed in [8], are not detected here : their angular positions would be, respectively,  $6.09 \text{ } 2\theta$ ,  $6.38 \text{ } 2\theta$ ,  $12.10 \text{ } 2\theta$ ,  $12.72 \text{ } 2\theta$ .

We shall now see that this apparent discrepancy is likely due to the crucial effect of the composition on the thermal behaviour of the i-phase. (The dodecahedral particles studied in [7] and [8] are considered to correspond to  $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$ .)

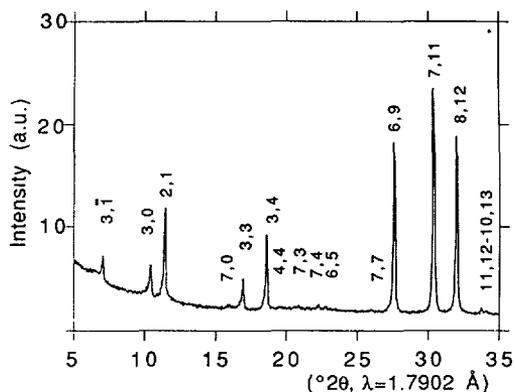


Fig. 5. — Same sample as figure 4. Smaller angle part of the X-ray pattern.

ii)  $\text{Al}_{62.3}\text{Cu}_{25.3}\text{Fe}_{12.4}$ . For this alloy there is no observable change in the diffraction pattern between 820 and 666 °C. Annealing down to 600 °C leads to a clear evolution of the tails of the peaks (Fig. 6) : the change in FWHM is rather small but the overall profile of the peaks is significantly modified : fits of the high-resolution diffraction peaks using Voigt or pseudo-Voigt lineshapes show that the profiles which are essentially Gaussian (G) at 666 °C transform to pure Lorentzian (L) at 600 °C. Using a Voigt function, the  $\text{FWHM}_G$  <sup>(2)</sup> is about  $0.019^\circ\theta$  at 666 °C (compared to a FWHM of  $0.025^\circ\theta$ ) and it becomes negligible at 600 °C. Using a pseudo-Voigt profile function, expressed as  $pV = xL + (1 - x)G$ , the mixing parameter  $x$  is equal to 0.2 at 666 °C and it becomes larger or equal to 1 at 600 °C, excepted for the (18, 29) line for which  $x = 0.8$ .

<sup>(2)</sup> According to the definition of Voigt function (convolution of Lorentzian and Gaussian functions), the FWHM is obtained from :  $(\text{FWHM})^2 = (\text{FWHM}_G)^2 / \text{Log } 2 + (\text{FWHM}_L)^2$ , where  $\text{FWHM}_G$  and  $\text{FWHM}_L$  are respectively the widths for the Gaussian and Lorentzian functions (Langford J. I., *J. Appl. Cryst.* 11 (1978) 10-14.

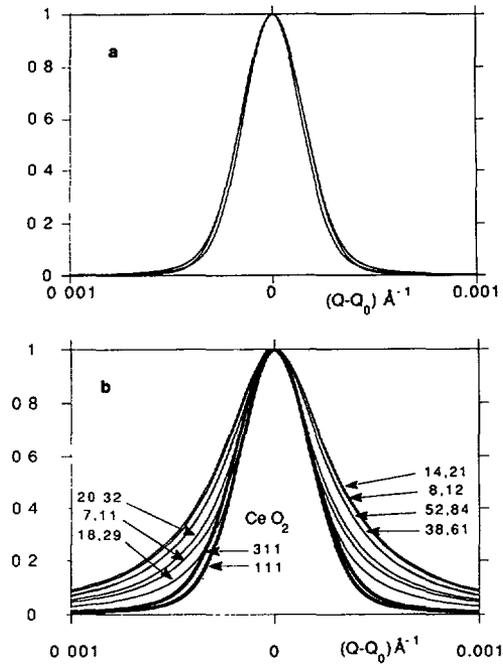


Fig. 6. — Thermal stability of the  $\text{Al}_{623}\text{Cu}_{253}\text{Fe}_{124}$  i-phase: lineshapes change from Gaussian to Lorentzian at  $600^\circ\text{C}$  (high-resolution experiment). a) Sample annealed for 2 h at  $820^\circ\text{C}$ , then 65 h at  $666^\circ\text{C}$ . The (N, M) values for the peaks reported on this plot are (7, 11) (8, 12) (38, 61) (18, 29) and (20, 32). The profiles are identical to the instrumental profile. b) Same sample as a) after further annealing at  $600^\circ\text{C}$  for 6 days. Two Bragg peaks from a standard  $\text{CeO}_2$  powder sample give the instrumental profile.

This unusual behavior ( $x > 1$ ) has been already reported for other materials (nickel oxide [15], barium fluoride [16]) and the corresponding profiles have been called « super-Lorentzian ». In this case, if the profile is fitted using a single pseudo-Voigt function there is a systematic discrepancy between experimental and fitted profiles at the peak maximum. An analysis with a superposition of two distinct pseudo-Voigt functions (corresponding to a bimodal distribution: narrow and broad) has been proposed to suppress this misfit [17]. In our case the use of two pseudo-Voigt functions does not improve the fit.

We can also notice that the width of the Lorentzian peaks roughly increase with the value of  $q_{\perp}$ . There are a few exceptions to this trend: although the peaks (18, 29) and (52, 84) correspond to nearly the same value of  $q_{\perp}$ , their corresponding widths in the « Lorentzian » state are clearly different (Fig. 6). Hence, a dependence on both the parallel and the perpendicular components of the 6D wave vector has to be considered.

The heights of the peaks presented in figure 6 have been normalized, in order to compare the profiles. In the actual spectra, the change in profile after annealing at  $600^\circ\text{C}$  is accompanied by a decrease in height of the peaks but at constant integrated intensity. The peaks are broadened symmetrically, with no displacement of their centers.

The change in profile occurs rapidly: an annealing time of a few hours at  $600^\circ\text{C}$  is sufficient to reach thermodynamic equilibrium. Indeed, we did not observe any further evolution by annealing at  $600^\circ\text{C}$ , even for 4 days. However, if the temperature is lowered to  $575^\circ\text{C}$ , the lineshape evolves: the peak width increases and small shoulders appear in the tails of the

(7, 11), (8, 12) and (20, 32) peaks. There is no further evolution at 550 and 500 °C. These effects disappear reversibly by annealing back for 1 hour at 750 °C.

Thus, it would appear that the heat-treatment at 600 °C has induced phason strain, but the long range quasiperiodic order is preserved. If the Lorentzian profile is considered as resulting from the superposition of a Bragg peak and diffuse scattering located in the wings, the Bragg intensities are reduced, analogous to a Debye-Waller factor dependent on both  $q_{\perp}$  and  $q_{\parallel}$ , and the lost intensity is recovered in the tails of the Bragg peaks, as strongly peaked diffuse scattering. This scheme is compatible with a random tiling model [1]. Also, the fact that the *i*-phase is better ordered at high temperature is consistent with entropy playing the dominant role in stability. However, a more straightforward lineshape analysis can be carried out in terms of defect broadening. A study by electron microscopy is underway in order to clarify the nature of the disorder. First results suggest an interpretation in terms of an imperfect lattice characterized by a broad distribution of defect-free distances : figure 7 shows physical evidence for a fragmentation of the grains by thin planar defects (analogous to stacking faults) lying in the fivefold planes.



Fig. 7. — Transmission electron micrograph of a  $\text{Al}_{62.3}\text{Cu}_{25.3}\text{Fe}_{12.4}$  sample annealed at 800 °C (2 h) then at 600 °C (18 h). The beam direction is parallel to a fivefold axis. The defects are lying in fivefold planes.

iii)  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  and  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$ . For these compositions, after annealing at 600 °C, there are shoulders in the tails of the Bragg peaks (Fig. 8). These shoulders develop when the annealing temperature is lowered with no variation of the total integrated intensity. The

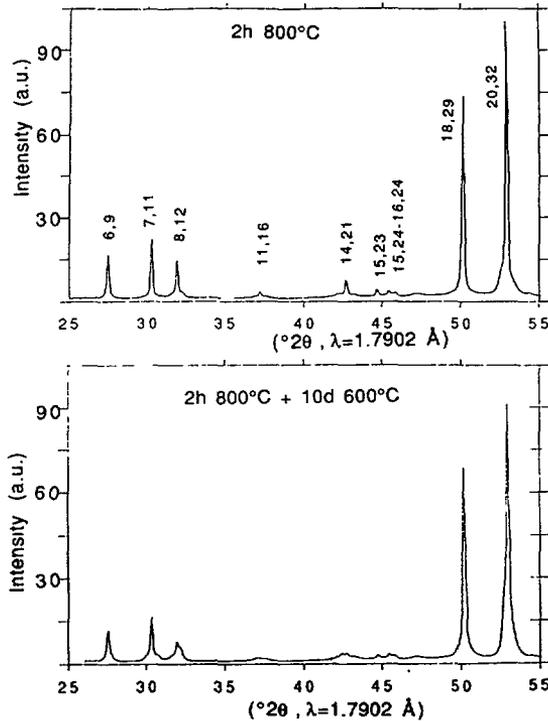


Fig. 8. — Thermal stability of the  $\text{Al}_{63}\text{Cu}_{25}\text{Fe}_{12}$  i-phase : the Bragg peaks have shoulders whatever the annealing temperature. The amplitude of the shoulders varies reversibly with temperature.

change in amplitude of the shoulders as a function of temperature occurs reversibly. The angular positions of both Bragg peaks and shoulders do not shift during the aging sequence. *The Bragg component of the scattering remains sharp.*

At 800 °C, the structural state depends on the composition : the  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  alloy is transformed into perfectly ordered i-phase by annealing above 700 °C (Fig. 9). On the other hand a smaller Fe content leads to samples which are never strictly « perfect » : the peaks have (more or less intense) shoulders whatever the annealing temperature, up to the solidus (Fig. 8). Thus, the transformation temperature is dependent on the composition.

Figure 9 shows that the amplitude of the effect is clearly  $q_{\perp}$  dependent. The amplitude of the shoulders increases with annealing time at constant angular position, and the Bragg peaks corresponding to large values of  $q_{\perp}$  finally disappear. They are replaced by peaked diffuse scattering, the maxima of which have angular positions clearly shifted from those of the ideal quasiperiodic phase (peak (8, 12) or (16, 24) in Fig. 9).

Some attempts have been made to allow the transformation to proceed to completion by prolonged annealing at 600 °C (Fig. 10). However the structural differences after annealing for 10 days and for 40 days can hardly be detected on the X-ray spectrum.

The nature of the structural transformation involved has not been established. The appearance of diffuse « side-bands » at about 600 °C could correspond to a structural transformation into a modulated quasicrystalline phase such as that observed by Audier *et al.* [7] in  $\text{Al}_{63.5}\text{Cu}_{24}\text{Fe}_{12.5}$ . However, an electron microscopy study on our « transformed » samples did not reveal splitting of the reflections into well defined satellites, there are only diffuse scattering streaks (see the electron diffraction pattern in Fig. 11). The modulated icosahedral

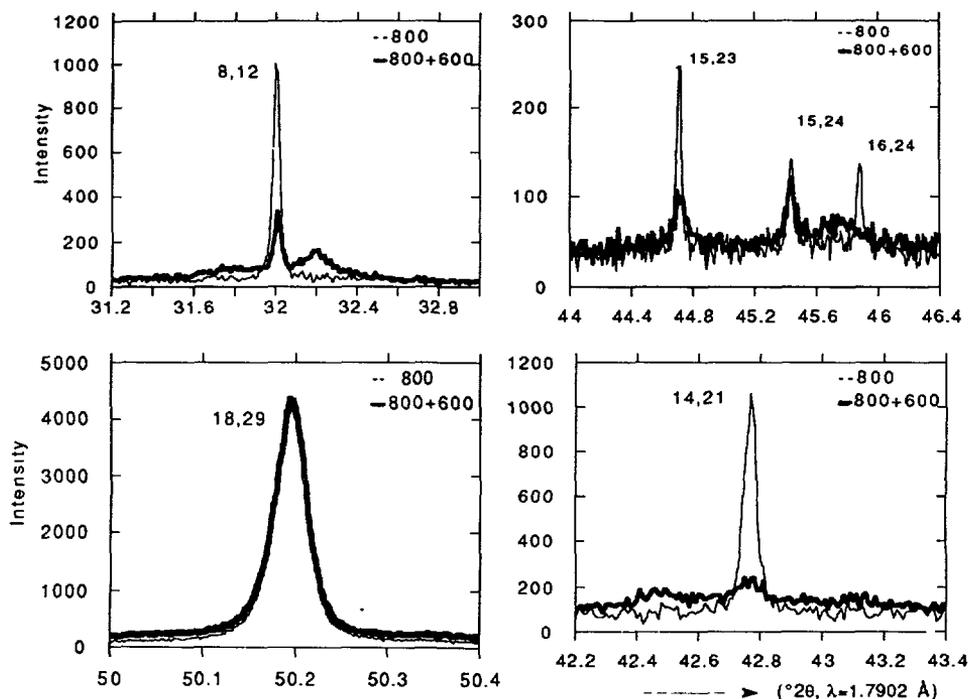


Fig. 9. —  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  i-phase : comparison of the X-ray spectra after annealing for 15 min at 800 °C and after further annealing for 4 h at 600 °C (high-resolution experiment).

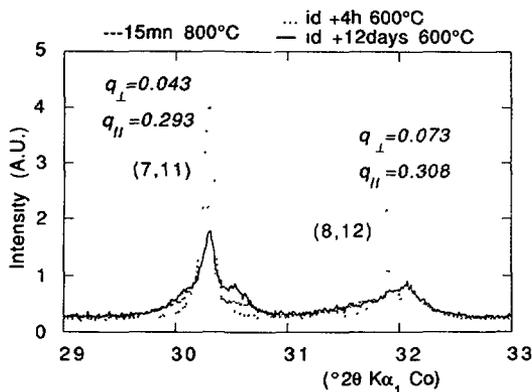


Fig. 10. —  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  i-phase : comparison of the X-ray spectra after annealing for 15 min at 800 °C and after further heat-treatments at 600 °C for 4 h and for 12 days respectively.

structure is considered as being an intermediate stage of an icosahedral-rhombohedral transition. It is described as an icosahedral structure modulated along its 5-fold axes with a pseudo-period of modulation equals to 130 Å [18]. On the high-resolution X-ray spectra, considering that every reflection has « side-bands » (mostly pairs), we have fitted the profiles in order to deduce the angular positions of the side-bands (Tab. I). If the side-bands are

Table I. — « Side-bands » in  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  annealed for 15 min at 800 °C, then 4 h at 600 °C (high-resolution experiment) : deviations ( $q_{\text{rhomb.}} - q_{\text{ico.}}$ ) from the quasiperiodic positions, compared with those calculated [20] for rhombohedral approximating structures corresponding to different rational approximations ( $p/q$ ) of the golden number. Details of calculation are given in reference [9].

| N, M   | $q_{\parallel}$<br>$\text{Å}^{-1}$ | $q_{\perp} \times 100$<br>$\text{Å}^{-1}$ | $\Delta q \times 10^3, \text{Å}^{-1}$<br>(measured)<br>$\pm 0.2$ | Splitting corresponding to<br>rhombohedral approximating<br>structures : $\Delta q \times 10^3, \text{Å}^{-1}$ |  |  |
|--------|------------------------------------|---|--|--|--|--|
|        |                                    |   |  | $a = 84.29 \text{ Å}$<br>$p/q = 8/5$   | $\alpha = 36^\circ$<br>$52.09 \text{ Å}$<br>$5/3$      | $32.20 \text{ Å}$<br>$3/2$                                 |
| 18, 29 | 0.474                              | 2.6                                       | - 1.06<br>1.59   | 0.021<br>- 0.212   | - 0.562<br>0.563                                       | - 1.473<br>1.477   |
| 7, 11  | 0.293                              | 4.3                                       | - 1.51<br>2.63   | - 0.339<br>0.357   | 0.913<br>- 0.910                                       | - 2.369<br>2.383   |
| 20, 32 | 0.498                              | 4.5                                       | - 1.92<br>2.09   | - 0.227<br>- 0.070<br>- 2.227<br>0.593   | 0.593<br>0.184<br>0.592<br>- 1.549                     | - 1.549<br>- 1.537<br>- 0.468<br>4.005                     |
| 6, 9   | 0.267                              | 6.3                                       | - 0.57<br>0.19   | - 0.132<br>- 0.303<br>0.170  | 0.317<br>0.792<br>- 0.440                              | - 2.045<br>- 0.829<br>1.222                                |
| 8, 12  | 0.308                              | 7.3                                       | - 2.25<br>1.69   | 0.356<br>0.112<br>0.356<br>- 0.956   | - 0.950<br>- 0.289<br>- 0.957<br>2.506                 | - 6.562<br>0.820<br>2.506<br>2.556                         |
| 14, 21 | 0.407                              | 9.6                                       | - 2.54<br>3.08   | - 0.109<br>- 0.799<br>- 0.926<br>0.889<br>1.198<br>- 0.109   | 0.306<br>2.104<br>2.414<br>- 2.322<br>- 3.134<br>0.295 | - 6.289<br>- 5.486<br>- 0.752<br>- 0.675<br>6.113<br>8.212 |

considered as satellites due to a modulated icosahedral structure, the order of magnitude of the splitting would correspond to a pseudo-period of modulation of about 500 Å.

Another interpretation would consist in considering the structure as two-phased (i-phase and approximating structure). Our many attempts of indexing in terms of approximating rhombohedral structures were unsuccessful. In particular the additional reflections cannot be attributed to the microcrystalline rhombohedral phase observed by Audier *et al.* (See, in Tab. I, the calculated splitting for  $p/q = 3/2$ ). Moreover, for these compositions, there is no evidence of a two-phased state in high resolution electron micrographs. There are only domain-like defects which constitute a mosaicity inside each grain (Fig. 11).

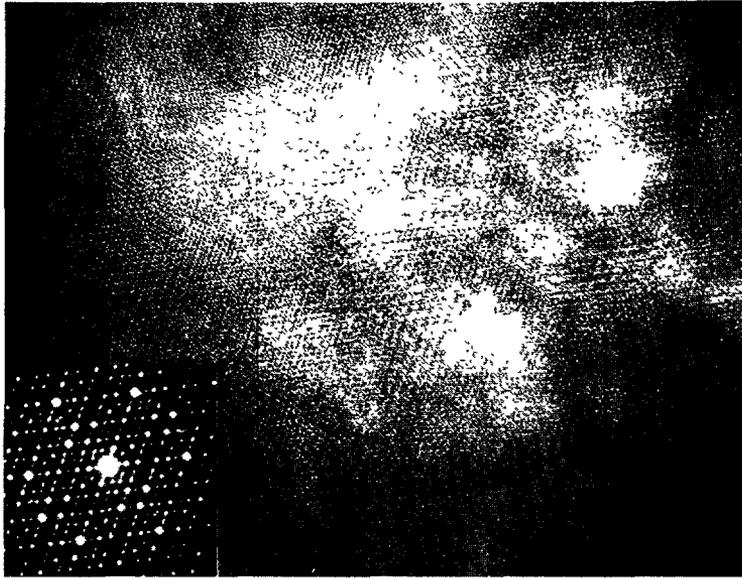


Fig. 11. — High resolution electron micrograph of a  $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  sample annealed at 800 °C (4 h) then at 600 °C (6 h) and 500 °C (6 h). The micrograph is taken with the incident beam parallel to the two-fold symmetry axis.

On the other hand the general evolution of the X-ray spectrum as a function of annealing temperature is similar to that observed by Goldman *et al.* [5] in melt-spun  $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$  samples except that there is *no actual broadening of the Bragg peaks*. This thermal behavior can be also compared with that observed by Bancel [6] during high temperature X-ray diffraction experiments on dodecahedral single grains removed from shrink cavities inside  $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$  ingots. Qualitatively the changes observed in the intensities of the Bragg peaks are similar *if the side-bands are not taken into account*. Finally, we think that the actual physical phenomena observed by us and by these authors are the same, and only the analysis of the results is different : in the experiment of Goldman *et al.* the resolution is not sufficient to exhibit the side-bands ; in Bancel experiment, the side-bands have been considered as thermal diffuse scattering and have been subtracted from the integrated intensity.

In order to investigate a possible « phase transition », two measurements by differential scanning calorimetry (DSC) were performed [19] : a first one on a perfectly quasiperiodic phase ( $\text{Al}_{63}\text{Cu}_{24.5}\text{Fe}_{12.5}$  sample annealed at 800 °C), the second one on samples « transformed » by annealing at 600 °C for 18 h. The two DSC scans are similar : *no sign of a phase transition has been detected up to 750 °C*.

### Conclusion.

The thermal behavior of the AlCuFe i-phase is very sensitive to the composition. In a small domain near  $\text{Al}_{62}\text{Cu}_{25.5}\text{Fe}_{12.5}$  a perfect quasicrystalline phase is stable down to low temperatures : this result qualifies the icosahedral phase for being a possible ground state in the phase diagram. Obviously, a structural transformation to a more stable crystalline structure at low temperature may not be ruled out, since the diffusion kinetics may simply be too slow to allow the transformation. For these alloys, there is no additional diffuse scattering in the X-ray spectrum, neither in the wings of the Bragg peaks nor elsewhere : this result does not support the random tiling model.

For small deviations from this domain of compositions, structural changes occur when the temperature is lowered. Depending on composition, peak profiles change: they become Lorentzian or diffuse shoulders appear in the tails of Bragg peaks, the global intensity remaining constant. The amplitude of these effects scales with  $q_{\perp}$ . The measured shifts do not correspond to a well defined rhombohedral approximating structure and there is no evidence of a phase transition. On the other hand, when the Bragg peaks become Lorentzian, transmission electron micrographs show that planar defects appear in the fivefold planes. A suggestion [21] is to consider the structural change at low temperature as a morphological transformation which would correspond to a freezing of high temperature thermal phasons into walls. The easy elimination of these defects would depend sensitively on the stoichiometry.

### Acknowledgments.

We wish to thank D. Gratias for invaluable discussions and comments.

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## Revue de livres

### Résolution numérique des équations aux dérivées partielles. Une première approche

Alain LE POURHIET

(Cépadues-Éditions, Toulouse) 1988, 390 p., 320 FF.

Il s'agit d'un cours donné en 4<sup>e</sup> année à Sup'Aéro. L'objectif est de donner un panorama général de la structure et des algorithmes pour résoudre numériquement sur ordinateur les équations aux dérivées partielles (EDP) usuelles. L'auteur se limite au cas linéaire. Le lecteur est supposé avoir en mémoire ses cours de Deug ou de Taupe (Bac + 2).

La présentation de la classification des EDP, leur mise sous forme canonique, la validation des schémas discrétisés de résolution, sont clairement discutées. Les propriétés spécifiques des grandes catégories (parabolique, hyperbolique et elliptique) sont fortement détaillées. L'ouvrage se termine par un exposé succinct de la méthode des éléments finis.

Au total, on a une présentation vieille d'au moins vingt ans d'un thème en pleine évolution. Les 4/5 des références ont un bon quart de siècle. L'auteur donne l'impression d'avoir très peu pratiqué son sujet. En fait, il eut été beaucoup plus utile de procéder à une approche « verticale », i.e. de se limiter à un problème important et de le traiter jusqu'au bout (l'algorithme de Godunov, par exemple), en allant jusqu'à l'organigramme. L'auteur semble ignorer que l'Analyse rigoureuse fait très bon ménage avec les traitements sur ordinateurs les plus élaborés. Un ouvrage sur les EDP, dans l'esprit de la série Dautray-Lions ou de celle de la collection Ciarlet-Lions (Masson), serait d'une très grande utilité à de futurs ingénieurs et physiciens.

Néanmoins, le présent ouvrage permet d'avoir sous la main un grand nombre de résultats très classiques, et présentés de manière agréable.

C. DEUTSCH.

### An Introduction to Solid State Diffusion

Richard J. BORG, G. J. DIENES

(Academic Press, San Diego 1988) 360 p., 49.50 \$.

Diffusion in solids controls many processes in material science, metallurgy, semiconductors physics, mineralogy, precisely all those processes in which the flow of matter is directly involved in determining the rate of modification of the properties of a solid. At the same time, diffusion is mainly related to the presence of defects in the structure, vacancies, interstitials, dislocations, grain boundaries and to their interactions. Many elementary phenomena, therefore, contribute to the mechanisms of diffusion, which are different in different systems.

Scientists from various branches are interested in this field, with a large production of practical information and theoretical results in the analysis of the various aspects of diffusion. Many specialized publications, books and review articles, report the fundamental principles or illustrate the results relative to particular systems, but very few are the textbooks for graduate students which describe in an appropriate way the principles and the main aspects of diffusion.

Indeed, to collect in a textbook the basic laws of diffusion and describe the properties that are controlled by mass transport in a variety of systems is not an easy task.

The authors of this book try this goal. Their experience in the field allows a clear presentation of many experimental results with a useful description of the difficulties and merits of the different experimental methods. Chapters deal with diffusion in metals and alloys, in ionic crystals, in semiconductors and with solid state reactions.

Unfortunately, the formal treatment of the theory and mathematics which form the basis for their experimental analysis is frequently, and surprisingly, confusing and affected by a lot of errors. The same first formula, defining the flow of matter, the deduction of the correlation coefficient, the description of the Boltzmann-Matano method, the introduction to the physics of semiconductors are the major examples.

G. BÖBEL.

### Modern Crystallography

édité par B. K. VAYNSHTEYN et A. A. CHERNOV

(Nova Science Publishers, Commack, N.Y., 1988) 395 p., \$ 119.

Cet ouvrage est la traduction en anglais du livre « Problemy Kristallografii » publié en 1987 par Nauka Publishing House.

Le titre anglais pourrait laisser penser qu'il présente une mise au point sur la cristallographie moderne, comme le traité « Modern crystallography » en quatre volumes publié de 1981 à 1988 par Springer Verlag (le titre russe de ce traité paru sous la direction de Vainshtein, Chernov et Shuvalov était : Sovremennaya kristallografia).

Le livre que nous analysons et qui pourrait s'appeler « Questions d'actualité en cristallographie » est un ensemble d'articles écrits par les cristallographes russes pour commémorer le centenaire de A. V. Shubnikov (1887-1970). Les contributions y sont regroupées en cinq ensembles qui correspondent presque aux quatre volumes du traité paru chez Springer :

#### **Théorie de la symétrie**

Principe d'égalité symétrique dans la croissance des macromolécules biologiques et des biocristaux par Vaynshteyn ; théorie de la symétrie de similitude : développements actuels par Zamorzaev et Zamorzaev ; nouvelles régularités de symétrie pour les concrétions cristallines par Shafranovskiy ; quatre règles de symétrie par Zheludev ; symétrie superfédorovienne des cristaux modulés moléculairement par Koptsik.

#### **Analyse structurale**

Effets de moiré et applications par Pinsker ; ondes X stationnaires par Afanas'ev et Imamov ; méthode algébrique pour interpréter la distribution de Patterson par Shchedrin ; structure de systèmes de cristaux liquides lyotropiques et de membranes biologiques à partir de données sur la diffusion aux petits angles des rayons X et des neutrons par L'vov et Feygin.

#### **Croissance des cristaux**

Transitions de phase rugueuse des cristaux d'hélium par Andreev, Babkin et Parshin ; croissance de monocristaux à partir d'un bain chauffé par induction dans un récipient froid par Borik, Lomonova, Osiko et Prokhorov ; l'épitaxie par faisceau moléculaire et la création de structures modulées de semi-conducteurs par Neizvestnyy, Rzhanov, Stenin et Shumskiy ; influence de la déformation élastique créée par les impuretés sur la concentration et le comportement des défauts ponctuels des semi-conducteurs par Mil'vidskiy, Rytova et Solov'eva ; formation homogène de cristaux dans les liquides et les couches amorphes par Skripov et Koverda.

#### **Transitions de phase dans les cristaux**

Transitions de phase dans les elpasolites par Aleksandrov, Voronov, Misyul' et Flerov ; transitions de phase ferroélectriques dans des perovskites complexes par Smolenskiy, Isupov et Pronin ; transformations de minéraux lamellaires dans des conditions hydrothermales par Frank-Kamenetskiy, Kotov et Goylo.

#### **Propriétés physiques des cristaux**

Optique cristalline de milieux gyrotropes et absorbants par Grechushnikov et Konstantinova ; théorie de champ autocohérent pour les ions d'impureté par Kulagin et Sviridov ; ondes naturelles dans les cristaux par Shamburov ; dispersion moléculaire de la lumière hors d'équilibre dans les cristaux

semiconducteurs piézoélectriques par Velichkina ; étude des propriétés mécaniques des cristaux à l'Institut de Cristallographie de l'Académie des Sciences par Regel'.

... Ce livre de 393 pages, illustré de 173 figures, s'intéresse ainsi à bien des branches de la cristallographie, de la physique cristalline et de leurs applications. La traduction anglaise en est correcte, mais la traduction à partir du russe de quelques noms français (P'er Kyuri, Brillouine, Mogen, Otier) ou étrangers (Shenflisa, Fridrikh, Fol'mer, Hovey, Bridzhmen, Vul'f ou Vul'fom, Bregg) surprend parfois le cristallographe.

En conclusion ce livre fournit un tableau intéressant des travaux actuels des cristallographes russes ; il doit trouver sa place dans une bibliothèque de cristallographie, à côté de traités plus systématiques qu'il ne peut, bien sûr, remplacer.

P. COULOMB.

### Neutrino Astrophysics

John N. BAHCALL

(Cambridge University Press, 1989) 567 pages, £ 14.95, \$ 24.95.

Science books are rarely both important and entertaining. This one is, and more besides. It is timely, coming after the observations of neutrinos from supernova SN1987A, and when the gallium experiments and the water detectors are starting to observe solar neutrinos. It is thorough, covering all aspects of a rapidly growing field ; and it is authoritative.

Bahcall can fairly claim to have invented the discipline of neutrino astrophysics by his work over many years using the standard solar model to predict the flux of neutrinos from the sun and their rate of reaction in  $^{37}\text{Cl}$  in the Homestake mine experiment of Davis *et al.* The solar neutrino problem is the central theme of the book, the fact that the Homestake experiment observes  $2.05 \pm 0.3$  SNU of interactions where the standard solar model predicts  $7.9 \pm 2.6$  (at 3 standard deviations). The SNU, the « solar neutrino unit », is equal to  $10^{-36}$  events per target atom per second. So far there is no firm evidence of where the calculation is wrong. There are thorough discussions of the assumptions involved in the three major parts of the calculation — nuclear fusion processes in the sun, the transmission of neutrinos from deep in the sun to the underground detector and their detection by scattering.

But the book is not a linear slog through one heavy topic after another. It begins with an overview chapter at Physics undergraduate level, written in unstuffy prose, stating the major points that are picked up in the later chapters and ending with a list of the commonest questions that the author has to answer when he gives colloquia about solar neutrino problem ; such as « Isn't it presumptuous to think that you can calculate the equation of state of matter in the solar interior to sufficient accuracy ? » or « Why was there only one experiment in 25 years ? » The answers are frank and uninhibited.

The later chapters do get technical, though the author's sense of fun breaks out when writing bibliographic notes — and his sense of the importance of science in human culture. For instance, citing A S Eddington's 1920 article on the internal constitution of the stars he says « Breathtakingly beautiful and insightful. No one can be a serious student of the subject without reading this paper. The paper also contains an astonishingly prophetic nonscientific statement. « If, indeed, the sub-atomic energy in the stars is being freely used to maintain their great furnaces, it seems to bring a little nearer to fulfillment our dream of controlling this latent power for the well-being of the human race — or for its suicide ».

Your reviewer, a particle physicist, found the astrophysical chapters on « Stellar evolution », « The standard solar model », « Nonstandard solar models » and « Stellar collapse » very clear and helpful. There are three chapters on the properties of neutrinos within the standard model of electroweak interactions. The description of matter oscillations by the MSW effect (invented by Mikheyev, Smirnov and Wolfenstein) is as clear as I have seen — though it is an intricate piece of formalism which can only really be understood by checking the calculations oneself. The chapter on possible time-variation of neutrino fluxes, did not convince me that any significant variations had been seen.

The part of the book I shall refer to most is the detailed review and comparison of the strengths and weaknesses of the new experiments, some of which are sensitive to the main neutrino flux from the sun

which must come from the interaction  $pp \rightarrow {}^2\text{H} + e^+ + \nu_e$ . It is extremely difficult to devise any solar model which does not link the rate of production of these neutrinos very directly to the heat output of the sun.

An illustration of the pervasiveness of this book is the fact that I recently found it on the desk of a colleague's PhD student in atomic physics. He is using new calculations of atomic opacities to challenge and check the underlying assumptions in Bahcall's solar model — and Bahcall has layed the arguments out so clearly that any such rival is led directly to the point of attack.

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