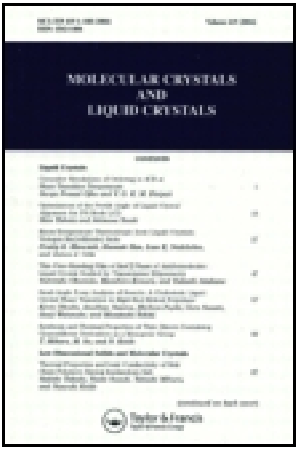

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Solid State Chemical Diffusion Between Naphthalene and 2-Chloronaphthalene

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SOLID STATE CHEMICAL DIFFUSION BETWEEN NAPHTHALENE AND 2-CHLORONAPHTHALENE

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Abstract Chemical diffusion studies between single crystals and polycrystalline samples of Naphthalene and 2-Chloronaphthalene were carried out at 315 K with annealing times varying from 300 to 2000 hours. Three techniques were used to determine the interdiffusion profiles : X-Ray diffraction, mass spectrometry and Raman microprobe spectrometry.
Interdiffusion coefficients are given, a function of the concentration of the solid solutions, for both polycrystalline and single crystalline samples. It is noted that metastable solid solutions can be formed by the irreversible process of interdiffusion. A brief discussion is devoted to the comparison between powder and single crystal results.

I - INTRODUCTION

Organic chemical diffusion studies may well provide new information concerning both the mobility of molecules in a chemical potential gradient and the nature of the lattice defects which allow this mobility within the solid. For such a study, the aim of which is essentially fundamental, we have chosen a simple case where the two derivatives which interdiffuse are able to give isostructural solid solutions in a large concentration range.

The binary system Nahpthalene - 2.Chloronaphthalene is characterized by two domains of miscibility separated by a zone of demixion; at the temperature of our interdiffusion study, the first domain extends from 0 to 1 % of 2.Chloronaphthalene. The second one is larger and extends from 44 to 100 % of 2.Chloronaphthalene. All the mixed crystals are monoclinic with $P2_1/a$ and Z = 2 as are the pure compounds[1].

II - EXPERIMENTAL

II.1 PREPARATION OF SAMPLES

Single crystals of Naphthalene and 2.Chloronaphthalene were joined on their (001) faces under a light pressure. For powder samples,pressed pellets of each pure component were first formed using a pressure of 50 M Pa and then coupled under a pressure of 100 M Pa. In both cases, the obtained interdiffusion couple was heated at 315 K with annealing times varying from 300 to 2000 hr. Five powder couples and four single crystalline ones were analysed.

II.2 DIFFUSION PROFILES MEASUREMENTS

Three methods have been used to determine the distribution of composition of the two sorts of molecules along the samples after the diffusion treatment.

II.2.1 X-Ray diffraction

A layer of about 0.5 mm has been removed from each side of the interdiffusion couple (parallel to the interdiffusion direction) in order to eliminate the effects arising from surface diffusion or contamination by vapour. The sample was then cut up into slices of 10 μm thick, perpendicular to the direction of diffusion. Each slide was analyzed by X Ray diffraction techniques. Three kinds of results may be so obtained :

- all slices of the interdiffusion zone consist in solid solutions (and not in mixtures of pure components).
- the composition of each solid solution can be determined from the positions of the diffraction lines using the calibration curve obtained when studying the equilibrium diagram.
- the width of the diffraction lines is directly related to the distribution of concentrations in the slice.

In the present case, we have observed that for each slice the divergence between the limit concentrations and the mean one z (molar concentration of 2-Chloronaphthalene) always within 0.05.

This homogeneity of the thin layers clearly indicates that grain boundary diffusion is not the principal way of migration of the molecules.

II.2.2 Mass spectrometry

The sectioning of the couple was done the same way as in the first case. Each slice was then analysed by mass spectrometry. A calibration was carried out with known composition standards. Relative intensities of the two peaks corresponding to m = 128 and m = 162 were used to determine the concentration of each slice with a precision varying from 0.01 to 0.05 according to concentration ranges.

II.2.3 Raman microprobe analysis

In this case the couple has to be cut into two parts parallel to the direction of diffusion. One of these is placed under the laser beam of a Raman microprobe using a sample holder with two perpendicular movments. The area irradiated by the laser beam is about 5 µm diameter. Raman spectra are registered all along the direction of diffusion by moving the sample step by step. A preliminary study had pointed out that the convenient peaks to be selected are respectively ν_1 = 355 cm^{-1} (characteristic of 2.Chloronaphthalene) and ν_2 = 520 cm^{-1} (common to the two pure components). Known composition standards have been used to establish the calibration curve ($I_{355}/I_{520} = f(z)$).

This method, the optimization of which is not perfectly achieved, has nevertheless the advantage of its high spatial resolution.

Furthermore, this analysis being non destructive, it allows us to get several diffusion profiles for a given diffusion couple and so to check the reproductivility of the diffusion profiles at different ordinates.

Using these three different ways of investigation allows us to get complementary information and then makes the proposed diffusion profiles more reliable.

III - RESULTS

III.1 DIFFUSION PROFILES

The diffusion profile relative to single crystal experiments is given in figure 1. It corresponds to the mean of four results obtained from four experiments respectively performed during t = 1152, 1212, 1508 and 2274 hours and then normalized by the λ variable ($\lambda = x/\sqrt{t}$ where x is the penetration referenced to the MATANO's plane.

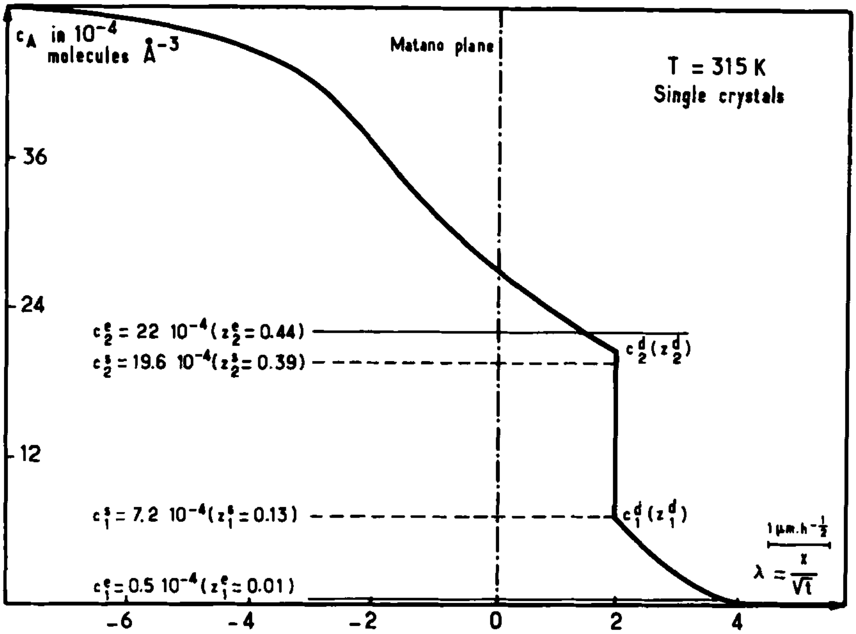

FIGURE 1. Diffusion profile (c_A = number of molecules of 2-Chloronaphthalene per Å^3).

III.2 METASTABLE SOLID SOLUTIONS

As expected from the equilibrium diagram two domains of mixed crystals separated by a gap of concentration are observed on the interdiffusion profiles. According to the equilibrium data, the concentrations of the solid solutions corresponding to the limits of the miscibility gap are respectively $z_1^e = 0.01$ and $z_2^e = 0.44$. But the concentrations of the two limit solid solutions observed here by the way of interdiffusion are closer than expected. It means that interdiffusion is able to give metastable solid solutions the limit compositions of which are near those of the spinodal points which are respectively $z_1^s = 0.13$ and $z_2^s = 0.39$. Such a formation of metastable phases has been previously

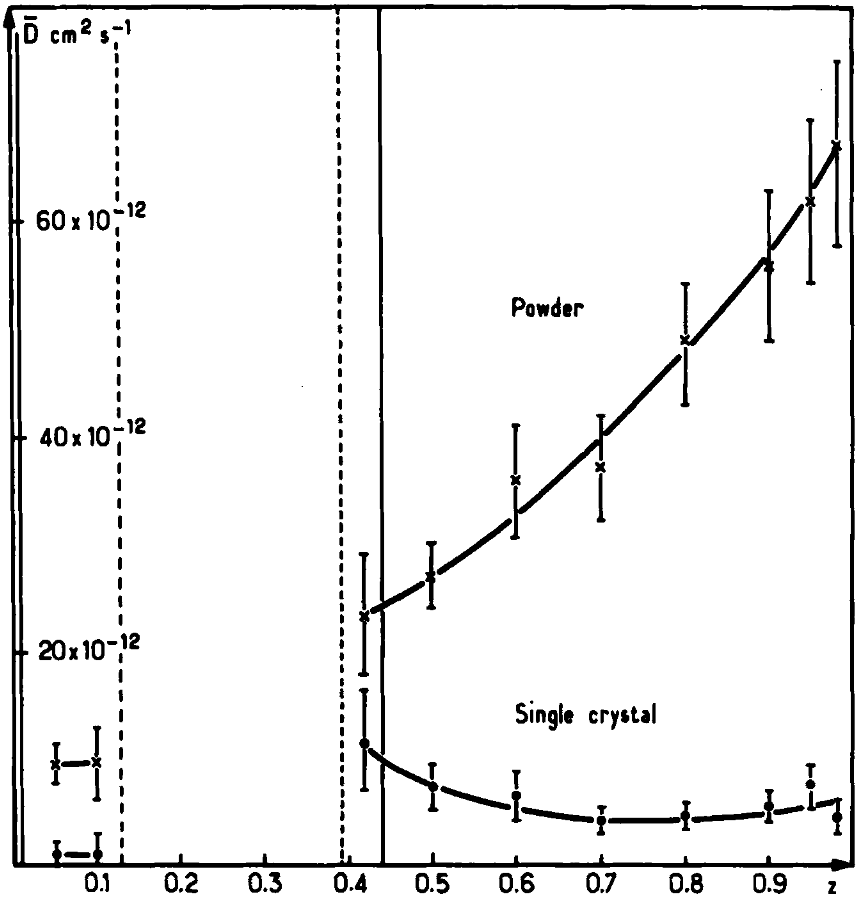

FIGURE 2. Variation of D̄ versus z.

observed in some chemical diffusion studies relative to metallic or ionic systems[2,3,4] .

III.3 DIFFUSION COEFFICIENTS

Figure 2 shows the variations versus z of the interdiffusion coefficients for both monocrystalline and polycrystalline samples.

Two main reasons can be proposed to explain, for a given concentration, the difference between the $\bar{D}$ characteristic of each sort of materials :

- in both monocrystalline and polycrystalline samples, the diffusion proceeds by a point defect mechanism. But, morever, in the case of powder couples, the existence of grain boundaries, which are important routes for diffusion, enhances the molecular mobility and thus the measured coefficient $\bar{D}$.

- A preliminary study[5] of the anisotropy of diffusion made on single crystals of naphthalene had pointed out that the diffusion coefficient measured perpendicular to the (001) plane seems to be the lowest one. In the polycrystalline samples where there is no preferred orientation for the grains, the measured coefficient corresponds to a mean value and thus is higher.

Experiments about anisotropy of diffusion are in progress in our Laboratory.

REFERENCES

1. A.Meresse, Thèse Bordeaux (1981).
2. A.Marwin and J.A.Pask, J.of Amer.Ceram.Soc., 54, 152 (1971).
3. J.D.Braun and G.W.Powell, Met.Trans. 4, 1207, (1973).
4. L.Bonpunt, N.B.Chanh, Y.Haget et M.Lahaye, J.Microsc. Spectrosc.Electron., 4, 651, (1979).
5. J.Meynard, These Bordeaux (1981).