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**Orientational glasses.****II. Calculation of critical thresholds in  $\text{ACN}_x\text{Mn}_{1-x}$  mixtures**Serge Galam<sup>(1)</sup> and Philippe Depondt<sup>(2)</sup><sup>(1)</sup> Groupe de Physique des Solides(\*) Tour 23, 2 place Jussieu, 75251 Paris Cedex 05, France<sup>(2)</sup> Département de Recherches Physiques<sup>(1)</sup>, Tour 22, 4 place Jussieu, 75252 Paris Cedex 05, France

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**Résumé.** — Une idée simple d'encombrement stérique permet de calculer des seuils critiques qui apparaissent dans le diagramme de phase de mélanges  $\text{ACN}_x\text{Mn}_{1-x}$ , où A représente K, Na ou Rb, et Mn, des atomes du type Br, Cl ou I. La concentration  $x$  du cyanure est divisée en une partie  $x_f$  de molécules libres de se réorienter, et une partie de molécules gelées  $x_i$ . Ce dernier terme  $x_i$  est calculé à partir des caractéristiques microscopiques des molécules concernées. Deux seuils critiques  $x_c$  et  $x_d$  pour la disparition respectivement des transitions et des domaines ferroélastiques sont obtenus. Les valeurs calculées sont en excellent accord avec les résultats expérimentaux disponibles. Des prédictions sont faites pour d'autres mélanges.

**Abstract.** — Using a simple steric hindrance based idea, critical thresholds which occur in the phase diagram of  $\text{ACN}_x\text{Mn}_{1-x}$  mixtures, where A stands for K, Na or Rb while Mn represents Br, Cl or I, are calculated. The cyanide density  $x$  is divided into a free-to-reorient part  $x_f$ , and a frozen-in part  $x_i$ . The latter term  $x_i$  is calculated from microscopic characteristics of the molecules involved. Two critical thresholds  $x_c$  and  $x_d$  for the disappearance of respectively, ferroelastic transitions and ferroelastic domains are obtained. The calculated values are in excellent agreement with available experimental results. Predictions are made for additional mixtures.

**1. Introduction.**

Pure alkali-halides  $\text{ACN}$ , where A stands for K, Na, or Rb, exhibit in cases for which experiments were done, a ferroelastic first order transition from cubic to lower symmetry at a temperature  $T_0$ . Cyanide orientations are disordered for  $T > T_0$  while ordered when  $T < T_0$ . Upon partial substitution of CN molecules with  $\text{Mn} = \text{Br}, \text{Cl}, \text{or I}$  molecules,  $T_0$  decreases to some value  $T_c$  at which the transition disappears.  $T_c$  occurs at a threshold value  $x_c$  of

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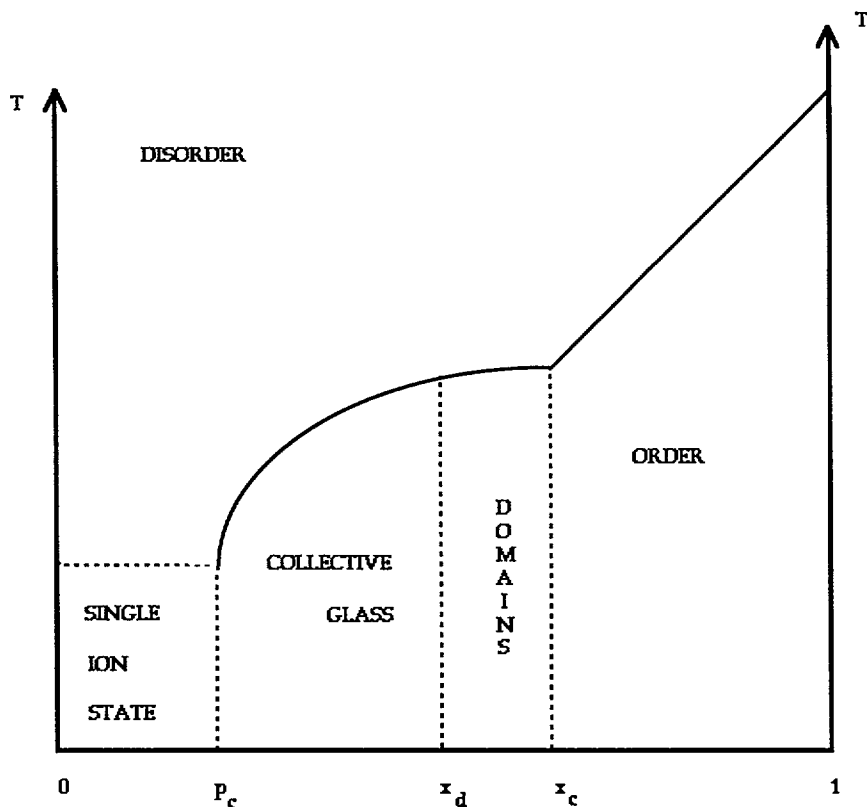


Fig.1. — Proposed phase diagram.

the cyanide concentration. Below  $x_c$ , there is experimental evidence of a local orientational freezing of cyanides, together with the absence of quadrupolar long range order. In parallel  $\text{ACN}_x\text{Mn}_{1-x}$  mixtures remain cubic at low temperatures. For a recent exhaustive experimental review, see [1].

Recently a random compressible spin system was proposed to describe the phase diagram of these mixtures [2] (hereafter noted as I). It showed that the problem is mainly a percolation problem, with however a discrepancy between the associated fcc percolation threshold  $p_c = 0.198$  [3] and the various experimental values of  $x_c$ . This result has been then interpreted as the signature of the non participation of some cyanides to the propagation of orientational long range order in the vicinity of  $T_0$ . Therefore the cyanide density  $x$  can be written as the sum of two parts: one free-to-reorient part  $x_r$  and a frozen-in part  $x_f$  with  $x = x_r + x_f$ . The latter term was calculated by hand in order that the free-to-reorient part  $x_r$  would coincide with the value  $p_c = 0.198$  at  $x_c$ . On this basis, a region of ferroelastic domains with random orientations was predicted, with no static phase transition below  $x_c$ . These domains were found to shrink, eventually to disappear at a new threshold  $x_d$  in the phase diagram (shown in Fig.1).

Shear torque experiments [4], as well as recent diffraction experiments [5] suggested a phase diagram very similar to that of figure 1. However at this stage, model I suffers from the *ad hoc* determination of  $x_f$  to obtain correct values for  $x_c$ . In this paper, a direct calculation of  $x_f$  from involved molecular volumes is done. From this microscopic calculation,  $x_c$  is a result

of the model, not an input as in I.

The paper is organised as follows. The random compressible model of I is reviewed in section 2. Section 3 deals with direct microscopic calculation of  $x_f$ , the density of frozen-in cyanide ions, due to substitution, for various substituted molecules. Values of  $x_c$  and  $x_d$  are obtained and compared to experimental data in section 4, together with concluding remarks.

## 2. Review of the random compressible model.

In I a simple spin system was proposed to describe the intermediate temperature range of the phase diagram of  $ACN_xMn_{1-x}$  mixtures. Cyanide rotational degrees of freedom are represented by classical Heisenberg spin variables  $\{S_i\}$ . Site dilution on the fcc cyanide lattice is associated with a random site variable  $\epsilon_i$  that is equal to one if site  $i$  is occupied by a cyanide and zero otherwise. We thus have  $\bar{\epsilon}_i = x$ , where the bar denotes a configurational average. Elastic degrees of freedom are introduced via the compressibility of the Hamiltonian. We have,

$$H_0 = - \sum_{\langle i,j \rangle} J_{i,j} \epsilon_i \epsilon_j S_i S_j + \sum_{\langle i,j \rangle} \varphi_{i,j}, \quad (1)$$

where

$$J_{i,j} = J_0 - (u_i - u_j)J, \quad (2)$$

and

$$\varphi_{i,j} = \frac{\varphi}{2} (u_i - u_j)^2, \quad (3)$$

with  $J_0$ ,  $J$ , and  $\varphi$  being positive constants. We are using decoupled one-dimensional chains to account for elasticity. Variables  $\{u_i\}$  represent CN or Mn ion displacements at sites  $i$  with respect to the pure ACN lattice.

The volume differences between cyanide molecules and substituting Mn atoms, together with concentration fluctuations are included in the Hamiltonian through anharmonic elastic terms [2, 6], i.e., a uniform term

$$H_U = - \sum_{(i,j)} 2h_L(1-x)(u_i - u_j), \quad (4)$$

and a local term

$$H_A = - \sum_{(i,j)} h_{ij}(u_i - u_j), \quad (5)$$

with  $h_{ij} = h_S(2x - \epsilon_i - \epsilon_j)$ .  $h_L$  and  $h_S$  are constants associated respectively with long and short range elastic effects.

Once elastic degrees of freedom are integrated out, the total Hamiltonian  $H_T = H_0 + H_U + H_A$  becomes, at zero external pressure,

$$H_e = -G \sum_{\langle i,j \rangle} \epsilon_i \epsilon_j S_i S_j - \frac{J^2}{2\varphi} \sum_{\langle i,j \rangle} (\epsilon_i \epsilon_j S_i S_j)^2, \quad (6)$$

where  $G = J_0 - \frac{2hJ}{\varphi}(1-x)$  and  $h = h_L - h_S$ .

The phase diagram associated with equation (6) has only one transition into one ordered phase. This transition disappears at the fcc site percolation threshold  $p_c$ .

The discrepancy between  $p_c$  and  $x_c$  is taken as the signature of some cyanides not participating to the propagation of long range order. On this basis we can write

$$x = x_r + x_f, \quad (7)$$

where  $x_r$  is the proportion of cyanides which are able to reorient and thus to participate to the propagation of long range order at low temperatures. In parallel  $x_f$  represents the orientationally trapped cyanides. This partial individual freezing appears as an additional effect of dilution. It is related to the shape difference between dumbbell-like cyanides and spherical Mn ions, which, indeed, was not taken into account in  $H_U$  and  $H_A$ .

If  $\alpha$  is the average number of cyanide ions which are orientationally frozen by one substituted Mn ion, it is reasonable to postulate for  $x_f$  the simple expression  $x_f = \alpha(1 - x)$ . The value of  $\alpha$  is then determined in order that the percolation of  $x_r$  coincides with  $p_c$ . Thus

$$\alpha = \frac{x_c - p_c}{1 - x_c} \quad (8)$$

Below  $x_f$  cyanide ions percolate but, the subset of CN ions which are free to reorient do not. This results in a phase constituted of ferroelastic domains. These domains shrink with dilution eventually to disappear at an additional threshold  $x_d$  determined from equation (7). Therefore the ferroelastic domain phase with no long range order exists in the range  $x_d < x < x_c$ . Such a phase was indeed found in experiments [4]. We have,

$$x_d = \frac{\alpha}{1 + \alpha} \quad (9)$$

The sketched phase diagram is shown in figure 1. It is worth stressing that in the range  $0 < x < x_d$ , equation (7) reduces to  $x = x_f$  with  $x_r = 0$ .

### 3. Direct microscopic calculation of $\alpha$ .

Model I produces a phase diagram supported by several experiments [1, 4, 5]. However it is based in part on the *ad hoc* calculation of  $\alpha$ , the average number of frozen cyanides. The present paper provides physical ground, from characteristics of the molecular compounds involved, to the approach of I. Values of  $\alpha$  are directly calculated from microscopic data.

In the pure ACN fcc crystal, the volume available to each ACN group can be divided into an occupied part  $v_o$  and a free part  $v_f$

$$v_{ACN} = \frac{a_{ACN}^3}{4} = v_o + v_f, \quad (10)$$

where

- $a_{ACN}$  is the lattice constant,
- $v_o = v_A + v_{CN}$ ,  $v_A$  and  $v_{CN}$  being volumes of ions, respectively alkali and cyanide ions, and
- $v_f$  is used in addition, by CN ions when reorienting.

The model supposes that a substituted Mn ion requires the lattice constant to be locally that of the pure AMn crystal, resulting in the volume change

$$\Delta v = \frac{1}{4} |a_{ACN}^3 - a_{AMn}^3|, \quad (11)$$

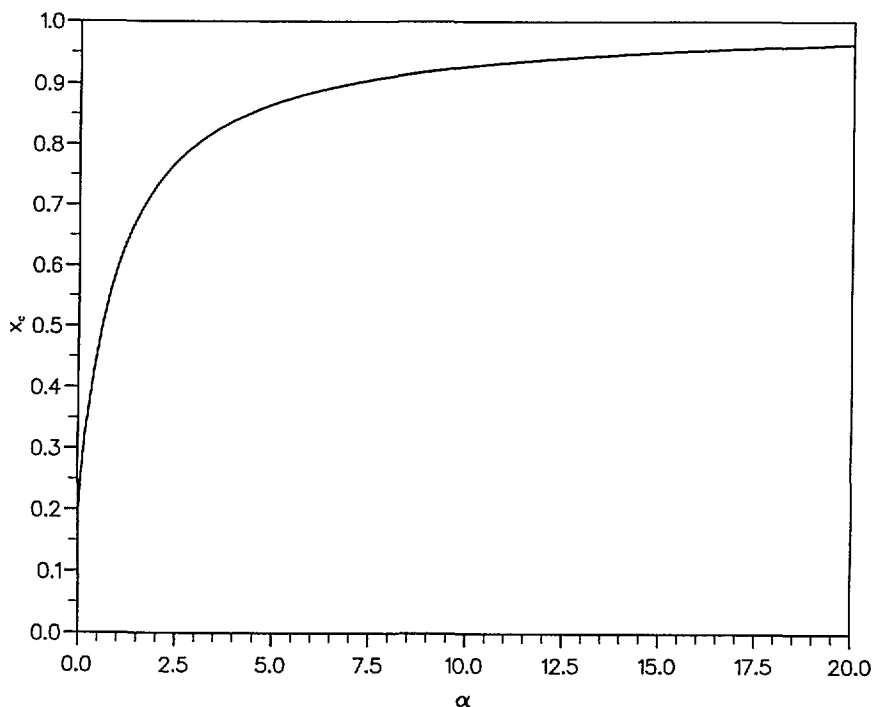


Fig.2. — Critical threshold  $x_c$  as a function of  $\alpha$ .

which is taken as an absolute value, since it is the deformation from the pure crystal which is considered. Moreover that local increment of volume is assumed to be balanced by an equivalent reduction of available free volume in the vicinity of the Mn ion. Available free space comes from local free volumes  $v_f$ .

However, each cyanide ion being surrounded by  $c$  neighbours, we assume that it is prevented from reorientational motion, through gear-like interactions, as soon as one of its  $c$  neighbours takes from it a volume  $v_f/c$ . Thus the average number  $\alpha$  of CN ions excluded by each substitution from propagating orientational long range order is the ratio of the local volume change to the volume each cyanide ion is capable of yielding before orientationally freezing,

$$\alpha = c \frac{\Delta v}{v_f} \quad (12)$$

Equations (8) and (12) yield for the critical threshold  $x_c$ ,

$$x_c = 1 - \frac{1 - p_c}{1 + c \frac{\Delta v}{v_f}} \quad (13)$$

The  $\alpha$  dependence of  $x_c$  is shown in figure 2. The domain size extension is given by

$$x_c - x_d = \frac{p_c}{1 + \alpha}, \quad (14)$$

where equation (9) is used for  $x_d$ . We can now confront this simple model to experimental reality.

Table I. — Numerical values calculated for  $\alpha$ ,  $x_c$ ,  $x_d$ , and  $x_c - x_d$  and experimental ones when known (denoted by 'exp.'). See details in the text.

ACN/AMn	$a_{ACN}(\text{\AA})$	$a_{AMn}(\text{\AA})$	$\Delta v(\text{\AA}^3)$	$v_f(\text{\AA}^3)$	$\alpha$	$x_c$	$x_d$	$x_c - x_d$
KCN/KCl	6.527	6.290	7.301	25.191	3.478	0.821 exp. 0.8	0.777 exp. 0.75	0.044
KCN/KBr	6.527	6.600	2.359	25.191	1.124	0.622 exp. 0.6	0.529 exp. 0.5	0.093
KCN/KI	6.527	7.060	18.459	25.191	8.793	0.918 exp. 0.9	0.898	0.020
NaCN/NaCl	5.890	5.630	6.471	12.672	6.128	0.887	0.860	0.028
NaCN/NaBr	5.890	5.970	2.110	12.672	1.998	0.732	0.666	0.066
NaCN/NaI	5.890	6.470	16.626	12.672	15.745	0.952	0.940	0.012
RbCN/RbCl	6.820	6.581	8.049	30.977	3.118	0.805	0.757	0.048
RbCN/RbBr	6.820	6.854	1.192	30.977	0.462	0.451 exp. 0.55	0.316	0.135

#### 4. Results and discussion.

Calculated values of  $\alpha$ ,  $x_c$  and  $x_d$  for several  $ACN_xMn_{1-x}$  examples are tabulated in the table. For comparison, the corresponding experimental values are also listed when available. The data used to obtain table 3. are:

- $a_{ACN}$  and  $a_{AMn}$  obtained from crystallographic data [7],
- $v_A = \frac{4}{3}\pi r_A^3$  where  $r_A$  is the radius of the  $A^+$  ion [8],
- $v_{CN} = 34.47\text{\AA}^3$  [9],
- $p_c = 0.198$  for the fcc lattice, and
- $c = 12$ , also for fcc.

Calculated values of  $x_c$  for  $A = K$  and  $Mn = Cl, Br$  and  $I$  agree remarkably well with the experimental ones [1, 10]. For  $RbCN_xBr_{(1-x)}$  mixtures, the agreement is less good, but it should be noted that  $\Delta v$  is then extremely small, which is bound to produce large relative errors. Finally, for the two examples for which  $x_d$  is known experimentally, the agreement is also very good.

We have thus presented an extremely simple model which reproduces known experimental results. At this stage, it is worth commenting the following basic features,

- One substituted Mn ion freezes, not its  $c$  cyanide neighbours but only a number  $\alpha$ . It may be pointed out that, in plastic crystals, even pure, the cubic lattice is only an average, the local environment of an ion being slightly different due to the lower molecular symmetry. It is then clear that the effect of a given substituted Mn ion should be non-cubic.
- The local volume change  $\Delta v$  is taken from  $\frac{vf}{c}$  regardless of whether Mn requires more ( $a_{AMn} > a_{ACN}$ ) or less ( $a_{AMn} < a_{ACN}$ ) space than the cyanide. This goes against the idea that a smaller Mn ion should provide extra volume instead of requiring more. However the lattice constant of the pure compound is a compromise between various constraints, hence the introduction of an impurity breaks this local equilibrium, thus requiring more

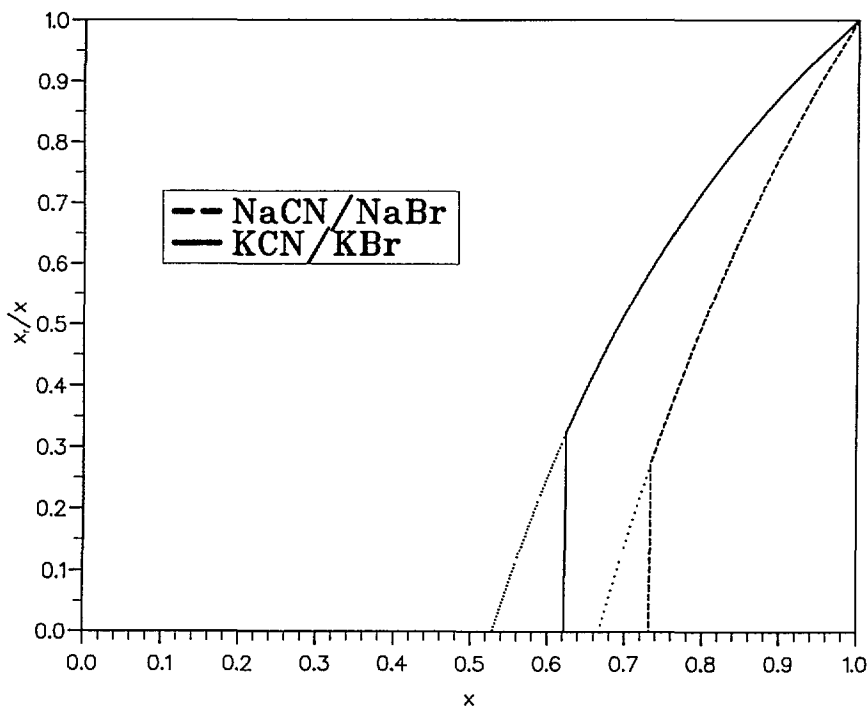


Fig.3. — Proportion  $x_r/x$  of free-to-reorient molecules as a function of  $x$ , for  $\text{KCN}_x\text{Br}_{1-x}$  ( $\alpha = 1.124$ ,  $x_c = 0.622$ ,  $x_d = 0.529$ ) and for  $\text{NaCN}_x\text{Br}_{1-x}$  ( $\alpha = 1.998$ ,  $x_c = 0.732$ ,  $x_d = 0.666$ ). The solid and dashed lines are for  $x > x_c$ , the dotted lines for the ferroelastic domain region  $x_d < x < x_c$ .

volume. Therefore it is the magnitude of the deviation from local equilibrium which is relevant and not its sign.

- The randomly oriented ferroelastic domain phase was found to exist in the range  $x_d \leq x \leq x_c$  with the width  $\frac{p_c}{1 + \alpha}$ . It is therefore the non-zero value of  $p_c$  which generates that phase. It means in particular that domains are created by the statistical fluctuations with respect to the Mn-mean field distribution which otherwise gives  $p_c = 0$  and then  $x_d = x_c$ . Figure 3 shows how the proportion  $x_r/x$  of free-to-reorient CN ions varies with  $x$  in the case of  $\text{KCN}_x\text{Br}_{1-x}$ . For  $x > x_c = 0.622$  the number of rotating ions decreases when substitution increases; the free-to-reorient molecules cannot percolate for  $x_d < x < x_c$ , and therefore are in domains that shrink with increasing substitution. When  $x < x_d$ ,  $x_r = 0$ , all CN ions are orientationally frozen.

To conclude we point out that the model makes predictions for compounds for which  $x_c$  is not yet known. It would be at this stage interesting to have more experimental results to check our predictions. In particular  $\text{NaCN}_x\text{I}_{1-x}$  seems different since in that case  $\alpha \simeq 16$  which is larger than  $c = 12$ . This result raises the question of whether second neighbours should be taken into account, and whether that should modify the model.

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