Diluted random fields
in
Mixed cyanide crystals

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Short title: Orientational Glasses
PA Classification Numbers: 64.60 A, 64.60 C, 64.70 P

Abstract

A percolation argument and a dilute compressible random field Ising model are used to present a simple model for mixed cyanide crystals. The model reproduces quantitatively several features of the phase diagrams although some crude approximations are made. In particular critical thresholds $x_c$ at which ferroelastic first order transitions disappear, are calculated. Moreover, transitions are found to remain first order down to $x_c$ for all mixtures except for bromine, for which the transition becomes continuous. All the results are in full agreement with experimental data.

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1 Introduction

Mixed cyanide crystals $X(CN)_{x}Y_{1-x}$ where $X$ is an alkali metal ($K$, $Na$ or $Rb$) and $Y$ stands for a spherical halogen ion ($Br$, $Cl$ or $I$) exhibit puzzling phase diagrams [1]. In particular the pure alkali-cyanide $XCN$ ferroelastic transition disappears at some cyanide concentration threshold $x_c$ which is not equal to the associated percolation threshold $p_c$. Moreover $x_c$ varies with both $X$ and $Y$ compounds. For instance, $x_c = 0.60$ and $x_c = 0.80$ for respectively $Y = Br$ and $Y = Cl$ with $X = K$.

Below $x_c$ experimental evidences hint to a cyanide orientational freezing, together with no long range quadrupolar order. In parallel, the high temperature cubic symmetry is preserved at low temperatures [1]. Analogies to spin-glasses and random field systems were suggested to elucidate the orientational glass state physical nature [1, 2].

In addition, while the transition stays first order for $X(CN)_{x}Cl_{1-x}$ [3], it was found to become continuous at $x_c$ for $X(CN)_{x}Br_{1-x}$ [4]. These experimental facts are still lacking an explanation.

The complicated symmetry of the molecules involved as well as the form of quadrupolar interaction make theoretical attempts rather difficult and heavy. Previous approaches [2 and references therein] tried to embody some of the molecule physical characteristics. However they failed to explain above features.

In this letter a model which combines a dilute compressible random field Ising system with a percolation argument is suggested to reproduce parts of the mixed cyanide phase diagrams. A microscopic calculation of critical thresholds $x_c$ is presented. Compressibility is found to produce a first order transition only at cyanide concentrations larger than a threshold $x_L$. On the opposite, diluted random fields are shown to activate a first order transition solely below another cyanide threshold $x_r$.

Transition orders which depend on the respective values of $x_c$, $x_L$ and $x_r$, are discussed for a large variety of mixtures. We predict transitions to remain first order down to $x_c$ for all mixtures, except in the case of bromine which exhibits a continuous transition at $x_c$. Our results fit perfectly a series of experimental data.

2 A percolation approach at $T = 0$

Starting from the $x_c \neq p_c$ experimental fact, we conclude that some cyanides do not participate in the propagation of quadrupolar long range order. These cyanides are thus “neutralized” from reorientation. Due to steric hindrance, a local deformation of the unit cell is expected on substituting one spherical $Y$ ion to the dumbbell-shaped cyanide. We assume that a local $XY$ unit cell, embedded in $XCN$ in bulk, matches the unit cell of $XY$ in bulk. The associated volume deformation of the former unit cell is $\Delta v = \frac{1}{4}(a_{KCN}^3 - a_{KX}^3)$.

From symmetry, each one of the $cY$ nearest neighbors is affected by this local volume deformation $\Delta v$. For a typical $XCN$ crystal with $Y = Cl$, the value of $\Delta v$ is calculated to be $\Delta v = \frac{1}{4}(a_{KCN}^3 - a_{KX}^3)$.
deformation which thus produces the overall volume deformation $\Delta V = c\Delta v$ ($c = 12$ and $p_c = 0.198$ on the fcc cyanide sublattice [5]).

$\Delta V$ may be extracted from neighboring unit cells using their free volumes which originate from volume differences between the unit cell and the molecule itself [6]. The free volume per molecule is $v_f = \frac{a_{XCN}}{4} - (v_X + v_{CN})$, where $a_{XCN}$ is the pure $XCN$ lattice constant, $v_X$ and $v_{CN}$ are ion volumes [7].

Dumbbell-shaped $CN$ reorientations are directly coupled to the unit cell shape via steric hindrance mechanisms. Any volume deformation of a cyanide cage (increase or decrease) lowers the corresponding symmetry which in turn lowers the number of accessible orientations. Here we are assuming that a cyanide whose cage is deformed (increased or decreased) becomes orientationally “neutralized”. Accordingly, one $Y$ substitution will affect on average,

$$\alpha = \frac{c|\Delta v|}{v_f},$$  \hspace{1cm} (1)

unit cells by deforming their respective free volumes. As a consequence, we obtain an effective density of free to reorient cyanides, $x_f = x - \alpha(1 - x)$. These free to reorient cyanides thus obey, by definition, site percolation with $x_{f,c} = p_c$ at $x = x_c$. Therefore we get,

$$x_c = \frac{p_c + \alpha}{1 + \alpha}. \hspace{1cm} (2)$$

Without a fitting parameter the calculation of $x_c$ is readily performed using crystallographic data [7, 8, 9]. The results are obtained for various mixtures (see the Table) including systems for which no experimental data are available. Below $x_c$ a region of randomly oriented ferroelastic domains with no static phase transition is predicted. These domains will shrink with increasing dilution to disappear eventually when $x_f = 0$ at a new threshold [10], $x_d = \frac{\alpha}{1 + \alpha}$. Shear torque experiments [11], as well as diffraction experiments [12] suggested a very similar phase diagram.

3 A crude Ising-like model

To extend above results to $T \neq 0$ we now build the simplest possible model Hamiltonian making several crude approximations.

- From symmetry, cyanides have several equivalent orientations making $q$-Potts variables appropriate [13]. However we restrict ourselves to the minimum number of orientations required to sustain an orientational long range order, i.e., two. Therefore we use Ising variables $\{S_i = \pm 1\}$ to mimic the cyanide orientational degrees of freedom.

- Cyanide quadrupolar interactions are long ranged. However our percolation argument is a short range effect. Therefore, to be consistent with above $T = 0$ calculation, we consider short range ferromagnetic couplings.
To fit the first order character of the pure XCN transition, we introduce elastic degrees of freedom in order to turn the continuous Ising ferromagnetic transition to first order. To keep calculations simple, we use an harmonic model of volume fluctuations though it is clearly a rudimentary model of elasticity [14].

Within a model of two equivalent orientations, a cyanide prevented from reorientation is trapped along one direction. To embody this effect, we introduce local quenched random fields. The probability \( p_t \) to have a local random field is equal to the probability of having a deformed cyanide cage. From the density \( x_t \) of trapped cyanide we obtain,

\[
p_t = \begin{cases} 
\frac{\alpha(1-x)}{x} & \text{if } x_d \leq x \leq 1 \\
1 & \text{if } x < x_d 
\end{cases}.
\]

The distribution function for the random filed \( h_i \) is then,

\[
P(h_i) = \frac{p_t}{2} \left[ \delta(h_i - h) + \delta(h_i + h) \right] + (1 - p_t) \delta(h_i).
\]

It satisfies both required symmetry conditions \( P(h_i) = P(-h_i) \) and \( \overline{h_i} = 0 \) (the overline denotes a field configurational average) which preserve the cubic symmetry of the associated problem.

4 The Hamiltonian

From above approximations, we obtain the following effective Hamiltonian,

\[
H_{\text{eff}} = -G \sum_{<i,j>} \epsilon_i \epsilon_j S_i S_j - \frac{E}{N^d} \left( \sum_{<i,j>} \epsilon_i \epsilon_j S_i S_j \right)^2 - \sum_i \epsilon_i h_i S_i,
\]

where \( G \) and \( E \) are constants, \( N \) is the total number of spins, \( d \) is the dimension [15], and \( \epsilon_i \) is a random site variable. It is 1 if site \( i \) is occupied by a cyanide and 0 otherwise. We have \( \{\epsilon_i\}_{av} = x \), where \( \{\ldots\}_{av} \) denotes a configurational average over site disorder.

We define the order parameter as \( m = \langle \epsilon_i S_i \rangle_{av} \) where averages are taken over both site and random field disorders. The associated mean field site free energy is,

\[
\mathcal{F} = \frac{1}{2} cGm^2 + \frac{3L}{4} m^4 - x k_B T \left\{ \frac{p_t}{2} \left[ \ln[cosh(\beta cGm + \beta Lm^3 + \beta h)] + \ln[cosh(\beta cGm + \beta Lm^3 - \beta h)] \right] \right\} + (1 - p_t) \ln[cosh(\beta cGm + \beta Lm^3)] - k_B T \ln(2),
\]

where \( \beta \equiv \frac{1}{k_B T} \), \( k_B \) is the Boltzman constant, \( T \) is the temperature and \( L = c^2 E \) (more details will be published elsewhere). In real systems \( h_i \) and \( \epsilon_i \) are
correlated. However, in order to be consistent with the previous short range interaction approximation, to keep the calculations simple and doing a mean field calculation, these correlations are neglected here. We now analyse two simple limiting cases which are physically meaningful.

4.1 The zero-steric hindrance effect case \((\alpha = 0)\)

From a Landau expansion of Eq. (6) a continuous transition occurs at the critical temperature, \(k_B T_c = x c G\) under the condition of a positive quartic coefficient, \(B = -\frac{L}{c G} + \frac{1}{3x^2}\), which results in the condition \(x < x_L\) on cyanide concentration [16] where,

\[ x_L \equiv \left(\frac{c G}{3L}\right)^{1/2}. \] (7)

At \(x = x_L\) the transition turns first order via a tricritical point \((B = 0\) with a positive free energy sixth order coefficient).

At \(x = 1\), \(p_t = 0\) (Eq. (3)) even if \(\alpha \neq 0\). From experimental works pure XCN exhibits a first order transition. All plastic systems must therefore satisfy \(x_L < 1\) with thus \(L > \frac{c G}{3}\). Dilution weakens the first order character of the transition. The associated negative quartic term \(B\) becomes smaller in amplitude to vanish eventually at a tricritical point \((x = x_L)\). There, the transition is continuous with tricritical exponents. Upon further dilution the transition becomes second-order with \(0 \leq x < x_L\).

4.2 The zero-compressibility case \((L = 0)\)

In this case, random field are acting alone \((\alpha \neq 0)\). At \(x = 1\), with \(p_t\) being an independent external parameter, the zero-compressibility free energy becomes identical to that of the trimodal random field Ising model [17]. A first order transition is found only for \(0.73 < p_t \leq 1\) and for some restricted range of random field intensities \(\sim 0.55 < \frac{h}{c G} < \sim 0.65\) [17]. These results produce an additional threshold in cyanide density around \(p_t = 0.73\) (Eq. (3)),

\[ x_r \equiv \frac{\alpha}{0.73 + \alpha}. \] (8)

Only at \(x < x_r\) can dilution turn the transition to first order via random fields. However condition \(x_c < x_r\) must also be satisfied since the transition itself disappears at \(x_c\). The equivalent constraint on \(\alpha\) gives,

\[ \alpha > \frac{0.73 p_c}{1 - 0.73 - p_c} \sim 2.09. \] (9)

Eq. (8) gives \(x_r = 0.60\) and \(x_r = 0.83\) for respectively \(K(CN)_x Br_{1-x}\) \((\alpha = 1.12)\) and \(K(CN)_x Cl_{1-x}\) \((\alpha = 3.48)\). In parallel the Table shows \(x_c = 0.62\) and \(x_c = 0.82\) for \(Br\) and \(Cl\) respectively. On this basis we conclude that upon dilution, while random fields can turn the transition first order in \(K(CN)_x Cl_{1-x}\) mixtures \((x_c < x_r)\), they cannot do it for \(K(CN)_x Br_{1-x}\) mixtures \((x_c > x_r)\).
5 Conclusion

In our model, both compressibility and random field drive the transition to first order. However, the compressibility effect weakens with dilution to fade out in the vicinity of $x_c$ for all systems. On the opposite, random fields start to be active at dilution below $x_r$, which is possible only when $x_r > x_c$. Using the condition $\alpha > 2.09$ (Eq. (9)), the Table shows it is always satisfied except for mixtures with bromine.

We can thus predict that dilution with chlorine and iodine maintains the transition first order down to $x_c$. Only bromine turns the transition continuous. A tricritical point is expected for $X(CN)_x Br_{1-x}$ mixtures. Our predictions reproduce experimental results with respect to potassium systems [3, 4]. Additional experiments on mixtures with sodium and rubidium would provide a definite ground to our model.

It was worth to stress that the extension of the model to $q$-Potts variables will not discard elasticity with respect to the first order character of the transition. Indeed, the rigid Potts model does exhibit a first order transition at $d = 3$, but only when $q > 2$. It is the case for $KCN$, but not for all systems. In particular, most materials which have a tetrahedral molecule in a cubic site will have equivalent orientations with $T_d$ symmetry, i.e., $q = 2$, like for instance the perchlorate tetrahedron in $KClO_4$. Therefore, elasticity is a necessary feature of our model.

Last but not least, the predictive power of our model comes as a surprise according to the several approximations made. In particular the short range character of the interactions is hard to justify. However, the results are impressive showing there must exist some screening mechanism which allows such a simple model.

Acknowledgments

I would like to thank Ph. Depondt, P. Doussineau and A. Levelut for stimulating comments on the manuscript.
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Table 1: Numerical values calculated for $\alpha$, $x_c$ and $x_d$ and experimental thresholds when known (denoted by 'exp:'). Units for lengths and volumes are å and å$^3$.

See details in the text. Error bars are within respectively ±0.01 for all data in the Table, and ±0.05 for experimental thresholds.

| $XCN/Y$ | $a_{XCN}$ | $a_{XY}$ | $\Delta v$ | $v_f$ | $\alpha$ | $x_c$ | $x_d$ |
|---------|-----------|---------|-----------|------|---------|------|------|
| KCN/Cl  | 6.53      | 6.29    | 7.30      | 25.19| 3.48    | 0.82 | 0.78 | 0.75 |
| KCN/Br  | 6.57      | 6.60    | 2.36      | 25.19| 1.12    | 0.62 | 0.60 | 0.53 | 0.50 |
| KCN/KI  | 6.53      | 7.06    | 18.46     | 25.19| 8.79    | 0.92 | 0.90 | 0.90 |
| NaCN/Cl | 5.90      | 5.65    | 5.99      | 12.67| 5.68    | 0.88 | 0.80 | 0.86 |
| NaCN/Br | 5.90      | 5.97    | 2.11      | 12.67| 1.99    | 0.73 | 0.67 |
| NaCN/KI | 5.90      | 6.47    | 16.63     | 12.67| 15.74   | 0.95 | 0.94 |
| RbCN/Cl | 6.82      | 6.58    | 8.05      | 30.98| 3.12    | 0.80 | 0.76 |
| RbCN/Br | 6.82      | 6.85    | 1.19      | 30.98| 0.46    | 0.45 | 0.55 | 0.32 |