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Isomorphous phase transition and orientational freezing in hexagonal mixed crystal $C_{70(1-x)}C_{60x}$. A pseudospin model

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Abstract. A four-state pseudospin model is constructed for the isomorphous phase transition hcp-2→hcp-1 in pure C_{70} and in C_{70}-rich mixed crystal $C_{70(1-x)}C_{60x}$. With the specific anisotropic pseudospin interactions adapted to the C_{70} crystal the model is equivalent to a two-state Ising model in a temperature-dependent field. Replica symmetric state of the model is shown to approach the critical point when the width of distribution of random fields and/or of random bonds increases. The temperature of the phase transition and the phase equilibrium temperature then are practically constant, whereas the experiment shows their strong decrease with x. The main effect of dilution resides in an x-dependence of the model parameters. Dilatometric data on the hexagonal $C_{70(1-x)}C_{60x}$ are used to fit these parameters. A metastable disordered phase subsisting below the phase transition is discovered in a range of the model parameters and is shown to be responsible for the macroscopic behaviour of the system. A good agreement with experimental data is obtained for the spontaneous strain and for the x-dependence of the hysteresis.

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1 Introduction

The high-temperature solid phases of the pure fullerene C_{70} are orientationally disordered and show one of the close packed structures: fcc (cubic, Fm3m) or hcp (hexagonal, $P6_3/mmc$) [1]. Both structures have been observed depending on the preparation procedures [2,3]. The samples grown from solution crystallize preferentially in the hexagonal structure hcp ($P6_3/mmc$) [4,5]. The orientational distribution of the C_{70} molecules is practically spherical in the high-temperature phase hcp-2. At about 337 K the crystal C_{70} undergoes a discontinuous phase transition in which the long molecular axes become ordered along the crystallographic direction (0001). The space group of the crystal does not change at this phase transition, whilst the ratio of the lattice constants c/a jumps abruptly from the value characteristic to spherical effective molecules: $c/a = 1.63...$ (hcp-2 phase) to the value corresponding to the shape of a single C_{70} molecule $c/a = 1.84$ (hcp-1 phase) [4]. Thus, the phase transition hcp-2→hcp-1 falls into the category of isomorphous phase transitions [6]. For symmetrical reasons, such phase transitions are either of first order or there is no transition at all, both situations being separated by a critical point [7].

It was found [8] that an admixture of more spherical and smaller molecules of C_{60} in the sample of hcp-2 phase of C_{70} strongly lowers the temperature of the phase transition and causes a peculiar behaviour to the jump of the spontaneous strain at the phase transition: the jump initially increases and then decreases with increasing concentration x of the C_{60} in the system $C_{70(1-x)}C_{60x}$. At the concentration $x \approx 0.08$ the first order phase transition disappears completely. This resembles the typical behaviour related with a critical point. On the other hand, the dilution of the quadrupolar molecules C_{70} with the spherical molecules C_{60} introduces a distribution of random fields and of random bonds. Such a dilution then should logically lead to freezing of the orientational disorder in analogy to the well studied mixed systems $KCN_{(1-x)}Br_x$ [9,10]. In the present work we address the question of the interplay between the critical point and the freezing of the disorder on the basis of the dilatometric data of reference [8].

The existing theoretical treatments of the orientational glasses mainly exploit analogies with diluted magnets [11], which undergo symmetry-breaking phase transitions usually of second order [12]. Much less known is the influence of random fields and random bonds on strongly first-order phase transitions. Reference [13] presents general considerations on the impurity-induced rounding of the symmetry-breaking phase transition of first order without, however, studying particular models of interactions.

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Potts models, which exhibit discontinuous phase transitions for sufficiently high number of states, have been shown to turn to continuous phase transition at strong enough random fields [14]. This behaviour resembles the tricritical point [6] occurring in symmetry-breaking systems. Nothing at all, to our knowledge, has been published on the effects of random admixtures in the case of first-order isomoprhous phase transitions. This actuated us to use the available experimental data on the system $C_{70(1-x)}C_{60x}$ and to treat them with the simplest possible model. The model is based on the idea of Pirc *et al.* [10].

In Section 2 we define the order parameters relevant in the isomorphous phase transition hcp-2→hcp-1 of pure C_{70} and of the mixed crystal $C_{70(1-x)}C_{60x}$. Because the order parameters are fully symmetrical the corresponding free energy contains new terms in comparison with the free energy of the fcc→$R\bar{3}m$ phase transition in the same material [15]. The form of the free energy given in Section 2 is independent of microscopic interactions. We show that the usual assumptions of Landau theory do not provide simple indications on the x-dependence of the free energy coefficients.

A strongly anisotropic pseudospin model presented in Section 3 and treated in the mean field approximation allows one to obtain the free energy adapted to the geometry and to the interactions in the hexagonal $C_{70(1-x)}C_{60x}$. Since our model markedly differs from isotropic models used in the existing theoretical analyses of quadrupolar disordered systems [10,12] we describe it in some detail. We show that when subject to random fields and random bonds the model approaches the critical point, without, however, a significant variation of the phase transition temperature. Thus, a phenomenological x-dependence must be introduced to comply with the very strong decrease in the transition temperature with increasing x observed in experiment [8]. The most important property of the model is that a free energy minimum describing the disordered phase can subsist to very low temperatures even without substitutional disorder. This corresponds to a metastable disordered phase detected in quite a number of materials (see Ref. [16] for examples). Our fits to the dilatometric data for $C_{70(1-x)}C_{60x}$ indicate how the dilution enhances formation of this low-temperature disordered phase. Kinetic reasons for possible discrepancies between the present model and experimental observations are discussed in Section 4.

2 Order parameters and Landau free energy for the isomorphous phase transition hcp→hcp in $C_{70(1-x)}C_{60x}$

2.1 Order parameters

The orientational order parameter in the phase transition hcp-2→hcp-1 of C_{70} is the average of the second-order Legendre polynomial

$$\eta = \langle P_2(\cos(\vartheta))\rangle = \left\langle \frac{1}{2}\left[3(\cos(\vartheta))^2 - 1\right]\right\rangle, \qquad (1)$$

where ϑ is the angle between the long molecular axis and the crystallographic direction (0001). The order parameter η is close to zero in the disordered phase hcp-2 and amounts to one in the completely ordered phase hcp-1.

Since the volume change at the phase transition is rather weak [17] the relevant elastic order parameter is a traceless strain corresponding to the variation of the c/a ratio mentioned in the Introduction

$$\varepsilon_{11} = \varepsilon_{22} = -\sqrt{2/3}\varepsilon/2, \quad \varepsilon_{33} = \sqrt{2/3}\varepsilon, \qquad (2)$$

with $\varepsilon = 0.0810807 \times \sqrt{3/2} = 0.099301...$ Here the strain is expressed in a rectangular coordinate system with the z axis parallel to the direction (0001). The second order elastic constant c_0 corresponding to the strain (Eq. (2)) reads

$$c_0 = (2/3)(c_{11}/2 + c_{12}/2 - 2c_{13} + c_{33}). \qquad (3)$$

The strain of equation (2) and the elastic constant of equation (3) are, in fact, a normal strain and an eigenvalue of the elastic constant matrix respectively, only in the case of an isotropic medium, where $c_{33} = c_{11}$, $c_{12} = c_{13}$ and $c_0 = (c_{11} - c_{12})$. The normal strains and the elastic constants for general medium are given in Appendix A. Away from the critical point the full softening of elastic constants is not to be expected so that equations (2, 3) are a good approximations.

2.2 Free energy expansion

The most general, invariant expansion of the free energy in terms of the fully symmetrical order parameters η and ε contains the terms of all possible orders. When limited to the order 4 in η and to the order 2 in ε the free energy reads

$$\begin{aligned} F(\eta,\varepsilon;T) = &- E\eta + \frac{1}{2}A(T - T_c)\eta^2 + \frac{1}{3}B\eta^3 \\ &+ \frac{1}{4}C\eta^4 + \frac{1}{2}c_0\varepsilon^2 - r\eta\varepsilon + K\varepsilon. \end{aligned} \qquad (4)$$

The quantity E is formally equivalent to an external field tending to align the long molecular axes parallel to (0001) direction. It is present in the expansion even in the absence of any external field due to the full symmetry of the order parameter. Similarly, the coefficient K is formally equivalent to an external stress and gives rise to a continuous variation of the deformation ε with temperature. Such a variation has been really observed in systems of the hcp symmetry [18]. The presence of the terms E and K together with the third-order term proportional to B, implies a possibility of a first-order phase transition or no transition *et al.* [7]. The boundary point of both situations corresponds to an isolated critical point at which the phase transition disappears. This is the only possible case of a second-order phase transition occurring without a change of symmetry. Solution of non-linear equations for minima of the free energy (4) [19] shows that the phase transition disappears when the coefficient E

is big enough. In the present case it would mean that an increase in the concentration x of the non-quadrupole molecules C_{60} should strengthen the field E. The expected effect of dilution is of course opposite: the dilution should impede the molecules' ordering. Thus, the simple Landau theory with x-dependent coefficients does not provide a plausible description of the disappearance of the phase transition in the mixed system $\mathrm{C}_{70(1-x)}\mathrm{C}_{60x}$. The reason for that lies in the very schematic temperature-dependence only included in the term $\sim A(T-T_\mathrm{c})\eta^2$. The pseudospin model of the next section implies a rather specific temperature-dependence of the free energy and removes this inconsistency.

3 Pseudospin model for hexagonal $\mathrm{C}_{70(1-x)}\mathrm{C}_{60x}$

The first step in the construction of a pseudospin model is to define a discrete set of orientational states the molecule can visit in the disordered phase. The states should correspond to minima of an effective one-particle potential. To model this potential we considered the elongated C_{70} molecule averaged over the rotations about its long molecular axis. The neighbouring molecules were replaced by effective spheres resulting from the orientational disorder. In Section 3.1 we show that the use of purely steric interactions does not reproduce the orientational distribution experimentally observed in the fcc phase of C_{70}. The correct predictions are obtained by addition of a charge distribution following from the electronic structure of the molecule. Application of the same interactions to the hcp structure produces a one-particle potential with four minima, one of them in the direction (0001) as required in the hcp-1 phase. In Section 3.2 we construct symmetry-adapted combinations of the occupation numbers of the states defined. The pseudospin interactions then are simplified (Sects. 3.3 and 3.4) in such a way that the mean field arises only when the molecules form close packed planes with the long molecular axes perpendicular to the planes. This is the only arrangement observed in C_{70}. Using the replica symmetric state we show in Section 3.5 that the effect of random fields or/and of random bonds is a narrowing of the hysteresis, *i.e.* a rounding of the first order phase transition without variation of the phase equilibrium temperature. Section 3.6 presents fits of the model parameters to the dilatometric data of reference [8].

3.1 One-particle orientational potential and definition of the pseudospin states

Each site in the hcp structure has twelve nearest neighbours, which form 6 octahedral and 8 tetrahedral spaces (Fig. 1). To study the simplest single-particle orientational potential of the C_{70} molecule in the hcp-2 phase we have replaced all the nearest neighbours by effective spherical distributions. The potential of interaction between the central molecule and each effective sphere then was chosen in a Lenard-Jones form $V(\theta) = A/[r-R_0(\theta)]^{12} - B/[r-R_0(\theta)]^6$, where r is the distance from the centre of the ellipsoid to the centre of the sphere and θ is the angle of the long molecular axis with the bond vector of the molecules' centres. The function $R_0(\theta) = 2r_0 + \Delta r[3\cos^2(\theta)-1]/2$ involves the average radius $r_0 = 3.8$ Å of the C_{70} molecule and the parameter $\Delta r = 0.41$ Å describing its deviation from the spherical shape [20]. The constants A and B were set in such a way that the distance $2r_0 + \sqrt[6]{2A/B} = 10.6$ Å was equal to the separation of the nearest neighbouring molecules C_{70} in the hcp-2 phase [2]. The line a in Figure 2 shows the angular dependence of the local potential of the elongated molecule placed at a site of the hcp structure and interacting with the neighbouring spheres in the manner defined above. The section for which Figure 2 has been made contains the directions (0001) and (1000) as indicated in Figure 1. There is a minimum of the steric potential for $\vartheta = 0$, *i.e.* for the molecule oriented in the (0001) direction. However, the absolute minimum occurs at the angle $\vartheta \approx 0.35\pi$ somewhat greater than the angle corresponding to the octahedral space $\vartheta = \arccos(1/\sqrt{3}) \approx 0.30406... \times \pi$.

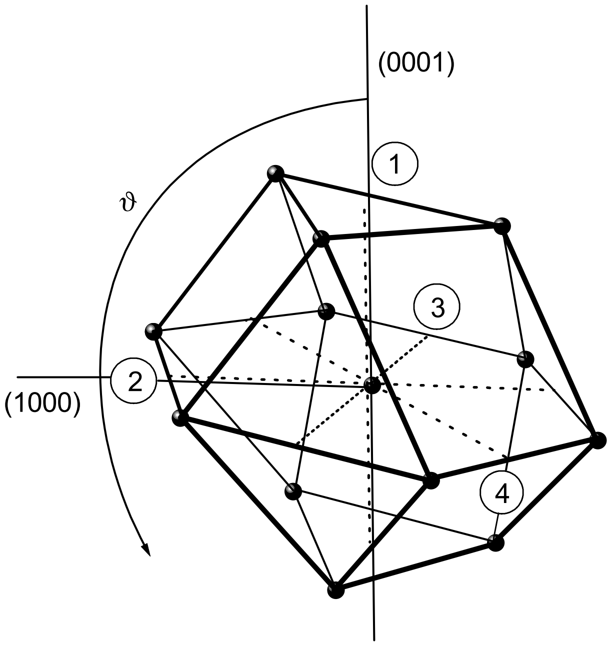

Fig. 1. Nearest neighbours of a node in hcp structure. Square faces of the coordination polyhedron are sections of octahedral spaces and triangle faces are sections of tetrahedral spaces. Dotted lines show the orientations of long molecular axis in states ①, ②, ③ and ④. Angle ϑ is counted from direction (0001) towards direction (1000).

When applied to the fcc geometry the above steric potential shows the absolute minimum exactly in the direction of the octahedral space, *i.e.* in the cubic direction (100). This contradicts the experimental finding [21], which shows a maximum of the one-particle orientational distribution in the (110) direction of the fcc phase. The latter result can be explained by correlated motions of the

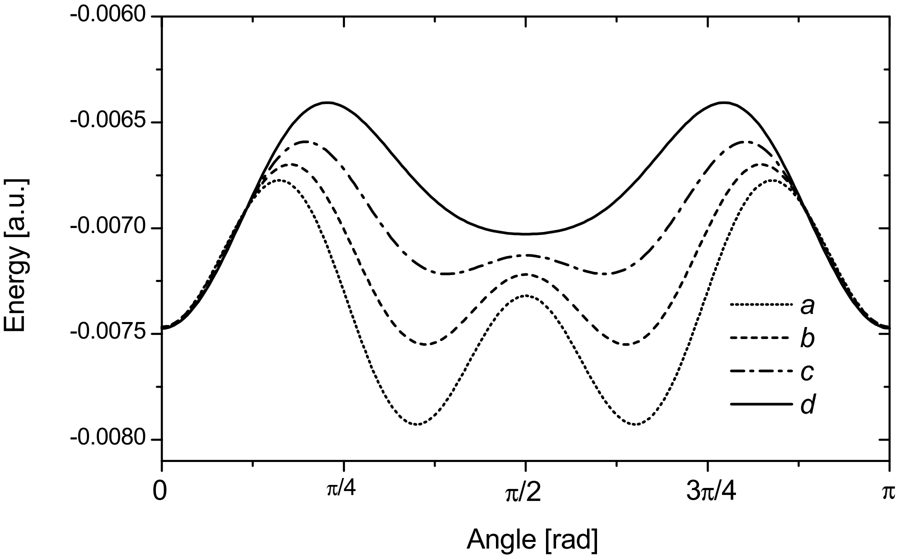

Fig. 2. One-particle orientational potential across section indicated in Figure 1 for purely steric interactions (*a*), and for interactions involving orientational polarizability of neighbours (*b*, *c* and *d*).

C_{70} molecules: whenever the long molecular axis points its nearest neighbour (this lies exactly in the (110) direction in the fcc structure) the neighbour tends to align perpendicular to the long axis of the central molecule. The most plausible energetic reason for such behaviour follows from the electric charge distribution in the C_{70} molecule. There are, namely, electron poor regions close to the poles and an electron rich equatorial stripe [20]. To model this we introduced a positive electric charge at each pole of the central C_{70} molecule and the corresponding compensating negative charge at the molecule's centre. The neighbouring molecules then would attract the poles of the central molecule by adopting the appropriate orientation. The lines *b*, *c* and *d* in Figure 2 show the resulting orientational potential across the section indicated in Figure 1 for three increasing values of the end charges. For the end charge strong enough the absolute minimum occurs at $\vartheta = 0$ and a single shallow side minimum at $\vartheta \approx \pi/2$, *i.e.* in the direction (1000).

The simplest pseudospin model based on the above observations involves the (0001) state ① and three states ②, ③ and ④ 120° away from one another in the plane $\langle 0001 \rangle$. Figure 1 shows schematically the orientational states of the present model. Introduction of additional states related to the double-well character of the potential near $\vartheta \approx \pi/2$ for some intermediate values of the end charges (see. Fig. 2) will not change qualitatively the results.

3.2 Symmetry adapted order parameters

Following the idea of Pirc *et al.* [10,22,23] we introduce four symmetry-adapted combinations of the occupation numbers $N_i = 1,\ 0$, where $i = 1,...4$, and label them by the irreducible representations of the site point group $\bar{6}m2\ (D_{3h})$:

$$\begin{aligned}
Z_1 &= N_1 - \frac{1}{3}(N_2 + N_3 + N_4) && (A_1') \\
Z_2 &= N_1 + N_2 + N_3 + N_4 && (A_1') \\
Z_3 &= \frac{1}{\sqrt{2}}(N_3 - N_4) && (E') \\
Z_4 &= \frac{1}{\sqrt{6}}(-2N_2 + N_3 + N_4) && (E'). \qquad (5)
\end{aligned}$$

The irreducible representations are given in the parentheses. In contrast to the cubic site symmetry considered in references [10,22,23], there are two linearly independent combinations belonging to the fully symmetrical representation A_1' here. The decomposition of the invariant subspace of the representation A_1' into the combinations Z_1 and Z_2 does not follow from symmetry and is in fact arbitrary. An advantage of the choice made in equation (5) is that the combination Z_2 constantly equals one at any state of the molecule and in any phase of the crystal. Consequently, the order parameter in the isomorphous phase transition hcp-2→hcp-1 involves the mean value of the combination Z_1 only.

The general Hamiltonian for the pseudospin-pseudospin interactions has the following form

$$H_{\text{pseudo}} = -\frac{1}{2}\sum_{i,j}\sum_{r,s} Z_{ri} J_{ij}^{rs} Z_{sj} \qquad (6)$$

with a 4×4 matrix J_{ij}^{rs}, $r, s = 1,...4$ for each pair of sites ij. The matrices J_{ij}^{rs} are symmetrical

$$J_{ij}^{rs} = J_{ij}^{sr} = J_{ji}^{rs}, \qquad (7)$$

which follows from the central symmetry of the C_{70} molecules averaged over the rotations about their long axes.

In the mean field approximation the Hamiltonian (6) becomes

$$H_{\mathrm{MF}} = -\sum_{i,j}\sum_{r,s}\langle Z_{ri}\rangle J_{ij}^{rs} Z_{sj} + \frac{1}{2}\sum_{i,j}\sum_{r,s}\langle Z_{ri}\rangle J_{ij}^{rs}\langle Z_{sj}\rangle \cdot \tag{8}$$

3.3 Anisotropic quadrupolar interactions, equation of state and phase equilibrium

When applying this kind of model to the mixed system $KCN_{(1-x)}Br_x$ the authors of references [10,22,23] assumed totally isotropic pseudospin interactions, *i.e.* all the matrices J_{ij}^{rs} diagonal with equal diagonal terms: $J_{ij}^{rs} = J_{ij}\delta_{rs}$. The same assumption was adopted in the majority of general theories on quadrupolar glasses [12]. Whereas this assumption might be justified in the case of the relatively distant CN^- ions, it is certainly false for C_{70}, where the molecules stick together. The simplification we adopt here stems from the observation that all the detected ordered phases of C_{70} consist of close packed hexagonal planes with the long molecular axes perpendicular to the planes. This is true for the ordered R$\bar{3}$m phase as well as for the hcp-1 phase. Interesting enough, a similar tendency occurs in the molecular ordering in the smectic A liquid crystals [24]. We then assume that the mean field at the site j has the general form $\sum_{i,r}\langle Z_{ri}\rangle J_{ij}^{rs} \sim \delta_{s1}$ and arises only when the neighbouring molecules are in the state ①, *i.e.* when $\langle Z_{ri}\rangle = \langle Z_1\rangle\delta_{r1}$ for each site i. With equation (7) in mind this is equivalent to the condition

$$\sum_i J_{ij}^{rs} = \delta_{r1}\delta_{s1}\sum_i J_{ij}^{11}, \tag{9}$$

which allows one to simplify the mean field Hamiltonian

$$H_{\mathrm{MF}} = -\sum_{i,j}\langle Z_1\rangle J_{ij}^{11} Z_{1j} + \frac{1}{2}\sum_{i,j}\langle Z_1\rangle J_{ij}^{11}\langle Z_1\rangle \cdot \tag{10}$$

The only relevant interaction parameters are now J_{ij}^{11}. In return, any long-range order with the molecules oriented in the states ②, ③ and ④ of Figure 1 is precluded. One easily sees that it is not possible to build a close packed plane with the molecules oriented in these states in the hcp structure. The condition (9) is as drastic as the assumption of the isotropic interactions but is better adapted to C_{70}. A less radical assumption implying a non-zero mean field for orientations other than ① might be more realistic, but would make the analysis much more complicated.

Taking into account the coupling with the strain and the full symmetry of the order parameters one arrives at the following mean-field Hamiltonian

$$\begin{aligned} H = &-\sum_{i,j}\langle Z_1\rangle J_{ij}^{11} Z_{1j} - h\sum_j Z_{1j} - r\varepsilon\sum_j Z_{1j} \\ &+ \frac{1}{2}\sum_j c_0\varepsilon^2 + \frac{1}{2}\sum_{i,j}\langle Z_1\rangle J_{ij}^{11}\langle Z_1\rangle \cdot \end{aligned} \tag{11}$$

(Note the normalization of the elastic constant c_0.)

There is a straightforward relation between the system defined by the Hamiltonian (11) and the usual two-state Ising model. This can be seen by adopting the transformation

$$Z_1 = (2s+1)/3 \tag{12a}$$

or

$$s = (3Z_1 - 1)/2. \tag{12b}$$

Whereas the variable Z_1 (Eq. (5)) takes the values 1 and $-1/3$, the corresponding values of s are 1 and -1. When written in the variable s the Hamiltonian (11) becomes

$$H = \sum_j\left(-\mathcal{H}\ s_j - \frac{1}{2}\bar{r}\varepsilon + \frac{1}{2}c_0\varepsilon^2 + \frac{1}{2}\bar{J}\langle s\rangle^2\right), \tag{13}$$

where the molecular field is

$$\mathcal{H} = \langle s\rangle\bar{J} + \bar{h} + \bar{r}\varepsilon, \tag{14}$$

while the renormalized parameters are

$$\bar{J} = \frac{4}{9}\sum_i J_{i1}^{11}, \tag{15a}$$

$$\bar{h} = \frac{2}{3}h + \frac{2}{9}\sum_i J_{i1}^{11} \tag{15b}$$

and

$$\bar{r} = \frac{2}{3}r. \tag{15c}$$

The constant terms have been dropped in equation (13) as only defining the absolute scale of energy. A further transformation

$$\varepsilon = \hat{\varepsilon} + \frac{\bar{r}}{2c_0} \tag{16}$$

and

$$\hat{h} = \bar{h} + \frac{\bar{r}^2}{2c_0} \tag{17}$$

allows one to write the Hamiltonian (Eq. (13)) in a simpler form

$$H = \sum_j\left(-\mathcal{H}\ S_j + \frac{1}{2}c_0\hat{\varepsilon}^2 + \frac{1}{2}\bar{J}\langle s\rangle^2\right) \tag{18}$$

with

$$\mathcal{H} = \langle s\rangle\bar{J} + \hat{h} + \bar{r}\hat{\varepsilon}. \tag{19}$$

The equilibrium values of the average $\langle s\rangle$ and of the strain ε are obtained by minimization of the free energy

$$F = -k_{\mathrm{B}}T\ln\Omega, \tag{20}$$

where the partition function Ω is

$$\Omega = \exp\left[\left(-\frac{1}{2}c_0\hat{\varepsilon}^2 - \frac{1}{2}\bar{J}\langle s\rangle^2\right)\Big/ k_\mathrm{B}T\right] \times \left[\exp(\mathcal{H}\ /k_\mathrm{B}T) + 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)\right]. \qquad (21)$$

The resulting self-consistent equations of state can be written in the following form

$$\langle s\rangle = \frac{[\exp(\mathcal{H}\ /k_\mathrm{B}T) - 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)]}{[\exp(\mathcal{H}\ /k_\mathrm{B}T) + 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)]} = \tanh(\overline{\mathcal{H}}/k_\mathrm{B}T) \qquad (22a)$$

$$\hat{\varepsilon} = \frac{\hat{r}}{\bar{c}_0}\langle s\rangle, \qquad (22b)$$

where

$$\overline{\mathcal{H}} = \mathcal{H} - k_\mathrm{B}T\ln(3)/2 \equiv \mathcal{H} + h_\mathrm{s}, \qquad (23)$$

while

$$h_\mathrm{s} = -k_\mathrm{B}T\ln(3)/2. \qquad (24)$$

Equation (22a) with equations (19, 23) and (22b) is formally equivalent to that for the usual two-state Ising model in an external field $\hat{h}+h_\mathrm{s}$. However, the field $\hat{h}+h_\mathrm{s}$ is here a result of intermolecular interactions and is allowed by symmetry; no external field is needed. This term would necessarily vanish for a symmetry-breaking phase transition. A particularity of the present model is that the field $\hat{h}+h_\mathrm{s}$ depends on temperature due to the 'entropic' contribution h_s (Eq. (24)). The dependence is a result of the triple degeneracy of the state $s = -1$.

Because of the presence of the field-like term $\hat{h}+h_\mathrm{s}$ the phase transition is generally of first order. The phase equilibrium occurs when the free energy (Eq. (20)) with equation (22b) inserted into equation (22a) is an even function of $\langle s\rangle$ and has two minima of equal depths. The condition for the free energy being an even function is

$$\hat{h} + h_\mathrm{s} = 0, \qquad (25)$$

which is equivalent to

$$T = T_\mathrm{eq} = \frac{2\hat{h}}{k_\mathrm{B}\ln(3)}; \qquad (26)$$

whereas the condition for the existence of two minima reads

$$T_\mathrm{eq} < T_\mathrm{ch} = (\bar{J} + \bar{r}^2/\bar{c}_0)/k_\mathrm{B}. \qquad (27)$$

The particular case of $T = T_\mathrm{eq} = T_\mathrm{ch}$ describes the critical point.

Whenever the condition (27) is fulfilled, the temperature T_eq (Eq. (26)) describes the equilibrium coexistence of phases.

3.4 Molecular field in diluted system

Equation (19) defines the molecular field acting on a given C_{70} molecule as a function of the quantity $\langle s\rangle$, which is the expectation value of s at a site occupied by a molecule C_{70}. Now in the diluted system $C_{70(1-x)}C_{60}$ only a fraction $(1-x)$ of sites are occupied by C_{70} and only these sites are involved in the creation of the molecular field. Therefore, the molecular field acting at a molecule depends on the volume average $\bar{s} = (1-x)\langle s\rangle$ rather than on the site expectation value $\langle s\rangle$:

$$\mathcal{H} = \bar{s}\bar{J} + \hat{h} + \bar{r}\hat{\varepsilon}. \qquad (28)$$

Inserting equation (28) into equation (22a) and multiplying both sides of the resulting equation by $(1-x)$ one obtains a self-consistent equation dependent on $\bar{s}$ only

$$\bar{s} = (1-x)\frac{[\exp(\mathcal{H}\ /k_\mathrm{B}T) - 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)]}{[\exp(\mathcal{H}\ /k_\mathrm{B}T) + 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)]} = (1-x)\tanh\left(\overline{\mathcal{H}}/k_\mathrm{B}T\right), \qquad (29)$$

where the relations (23) and (24) have been applied. The deformation of the sample is also proportional to the volume average $\bar{s}$, so that the analogue of equation (22b) now is

$$\hat{\varepsilon} = \frac{\hat{r}}{c_0}\langle \bar{s}\rangle\ \cdot \qquad (30)$$

One can easily check that equations (29, 30) are consistent with the minimum condition of the free energy (Eq. (20)) with the following one-particle partition function

$$\Omega = \exp\left[\left(-\frac{1}{2}c_0\hat{\varepsilon}^2 - \frac{1}{2}\bar{J}\bar{s}^2\right)\Big/ k_\mathrm{B}T\right] \times \left[\exp(\mathcal{H}\ /k_\mathrm{B}T) + 3\exp(-\mathcal{H}\ /k_\mathrm{B}T)\right]^{(1-x)}. \qquad (31)$$

The critical temperature T_ch now becomes

$$T_\mathrm{ch} = (1-x)\left(\bar{J} + \frac{\bar{r}^2}{c_0}\right)\Big/ k_\mathrm{B}. \qquad (32)$$

A noticeable property of the present model is that the first order of the phase transition results from the field-like term $\hat{h}+h_\mathrm{s}$ in equations (19, 28) and not from a non-linear coupling of the order parameter with strain as is required in symmetry breaking phase transition [6].

3.5 Effect of random fields and of random bonds

In addition to the numerical proportionality of the volume average $\bar{s} = (1-x)\langle s\rangle$ discussed above, the presence of admixtures in a system with orientational degrees of freedom introduces random fields and random bonds [9,10,22,23]. If the phase transition in the non-diluted system is of second order the critical temperature lowers with increasing amplitude of random fields and with increasing distribution width of random bonds [11]. The resulting phase is

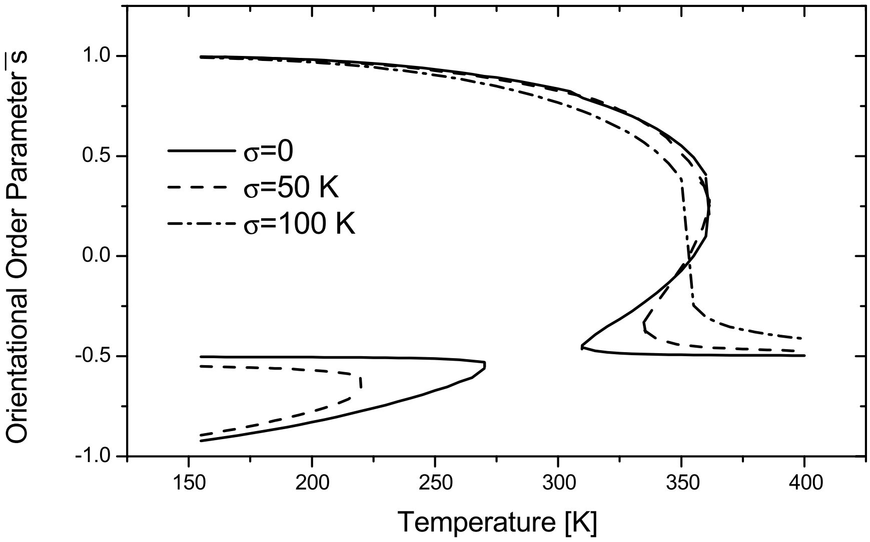

Fig. 3. Temperature dependence of orientational order parameter (Eq. (33)) at presence of random bonds and random fields with distribution width σ.

replica-symmetric [11] provided that the random amplitudes are not too strong. The replica-symmetric state in the present case is obtained by replacing the self-consistent equation (29) by the following equation

$$\bar{s} = \frac{(1-x)}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}z \mathrm{e}^{-z^2/2} \tanh\left(\frac{\sigma z + \overline{\mathcal{H}}}{k_{\mathrm{B}} T}\right), \qquad (33)$$

where $\sigma = \sqrt{q_{\mathrm{EA}} T_q^2 + T_{\Delta}^2}$, while q_{EA} is the Edwards-Anderson order parameter [11], T_q is the width of the random bonds distribution and T_{Δ} is the width of the random fields distribution (see Ref. [25] for analogous formula in the case of a first order phase transition governed by a non-linear coupling with the strain). Figure 3 shows the order parameter $\bar{s}$ calculated with equation (33) for the parameters of the model: $c_0 = 7875000$, $\bar{J} = 39.0$, $\bar{r} = 52500$, $\hat{h} = 195$ corresponding to the pure C_{70} and for three values of the total width σ. Although a precise x-dependence of the parameter σ is not straightforward [12,13] one should expect it to be an increasing function. Figure 3 shows that the main effect of the random fields and of random bonds is a narrowing of the hysteresis with practically no variation of the coexistence temperature. Now that the experiment shows a strong decrease in the transition temperature with increasing x the principal effect of the dilution lies in an x-dependence of the parameters of the model.

3.6 x-dependence of the model parameters for $C_{70(1-x)}C_{60x}$

The transition temperature hcp-2→hcp-1 in the mixed crystal $C_{70(1-x)}C_{60x}$ drops linearly with the concentration x of C_{60} at the rate ~20 K/%C_{60} both at cooling and heating [8]. The temperature of the transition at cooling is lower from that obtained at heating due to a hysteresis but the rate is alike in both cases. Therefore, the field $\hat{h}$ must depend on x so that $\partial T_{\mathrm{eq}}/\partial x = -2000$ K (Eq. (26)). Because of the presence of the temperature dependent field h_{s} (Eq. (24)) the field $\hat{h}$ now decreases with x in contrast with the predictions of the simple Landau theory (see Sect. 2.2 and Ref. [19]).

For $x = 0$ the model describes the isomorphous phase transition in the pure hexagonal C_{70}. Since the experimental spontaneous strain is $\hat{\varepsilon} \approx 0.01$ in this case we put $\hat{r}(x = 0)/c_0 = 0.01 \times (2/3)$ (see Eq. (30)). Further, we assume that the hysteresis observed in this phase transition between 308 K–364 K extends over the whole range of metastability of both phases. This assumption is in fact fulfilled for experiments done at an infinitesimally slow temperature variation. As a result we obtain (Eqs. (26, 27)): $T_{\mathrm{eq}}(x = 0) = 355$ K, $T_{\mathrm{ch}}(x = 0) = 389$ K and $\hat{h}(x = 0) = 195$ K. The equations for the limits of hysteresis allow us to calculate the parameters $\bar{J}$ and $\bar{r}^2/c_0$ for $x = 0$.

The value $\bar{r}^2/c_0(x = 0.088)$ can be obtained from $T_{\mathrm{eq}} = T_{\mathrm{ch}}$ (Eq. (27)) assuming that the concentration $x = 0.088$ corresponds to the critical point. It turned out, when solving numerically equations (29, 30), that a linear dependence of the parameter $\bar{r}$ on x produces a narrowing of the hysteresis much stronger than that observed experimentally [8]. A better fit has been obtained with a quadratic x-dependence of the quantity $\bar{r}/\sqrt{c_0}$. Since the x-dependence of the "bare" elastic constant c_0 is not known we assume a constant value here. In summary, the resulting set of the quantities (in kelvins) involved in the self-consistent equations (29, 30) are:

$$\begin{aligned} c_0 &= 7875000 \\ \bar{J} &= 39.0 \\ \bar{r} &= 52500 - 2460937.5x^2 \\ \hat{h} &= 195 - 1098.56x. \end{aligned} \qquad (34)$$

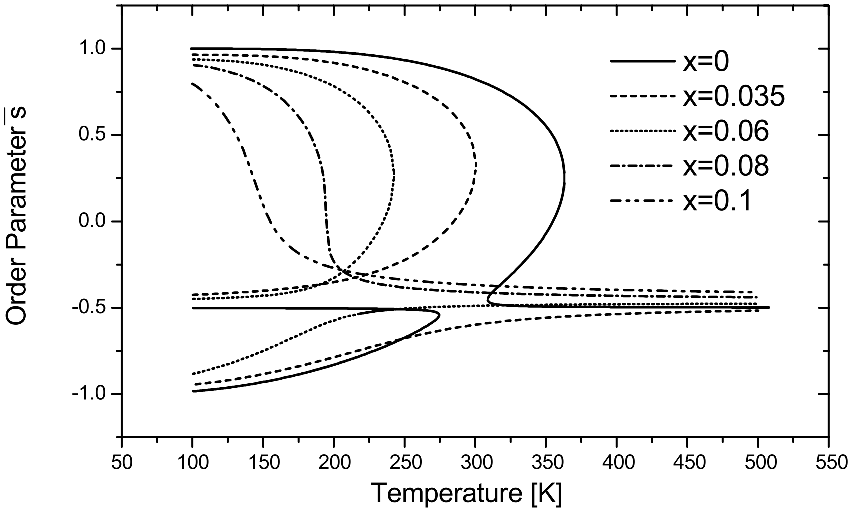

Fig. 4. Temperature dependence of orientational order parameter $\bar{s}$ evaluated from equations (29, 30) with parameters of equations (34).

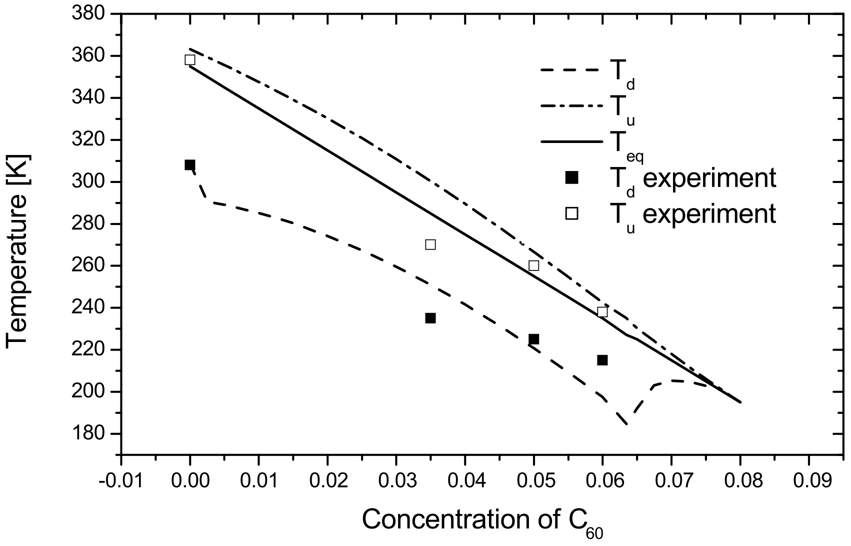

Fig. 5. Upper and lower limits T_u and T_d of hysteresis and phase equilibrium temperature T_{eq} as predicted by pseudospin model (Eqs. (29, 30) and (34)). Experimental points extracted from reference [8] are reported.

Figure 4 shows the temperature dependence of the orientational order parameter $\bar{s}$ obtained numerically from equations (29, 30) with the values from equation (34) for the concentrations x which were used in the dilatometric study [8]. An interesting and unexpected result is that the metastable phase with negative $\bar{s}$ reappears below 275 K in addition to the stable ordered phase with $\bar{s} \approx 1$ for $x = 0$. The metastable phase is represented in Figure 4 by the lowest branch of the continuous curve. For $x = 0.035$ and $x = 0.06$ the metastable phase subsists in the whole temperature range as a smooth continuation of the high-temperature disordered phase. In Figure 5 the lower and upper limits of the hysteresis T_d and T_u as well as the phase equilibrium temperature T_{eq} are shown as functions of the concentration x. In the case where the metastable phase subsists in the whole temperature range the lower limit of hysteresis is defined by the minimum of the free energy barrier (Eq. (20)) separating the metastable phase from the stable one. This explains the cusps in the curve $T_d(x)$ in Figure 5.

Figure 6 represents the behaviour of the spontaneous strain for the concentrations x from Figure 4. The limits of hysteresis are also marked. Figure 7 gives the same results normalized to $\hat{\varepsilon}(T = 300\ \text{K})$ as it was done in the dilatometric study [8]. The spontaneous strain in the disordered phase drops with decreasing temperature in the vicinity of the phase transition. This behaviour has been observed experimentally. Moreover, it explains in a natural way the initial rise and the subsequent decrease in the jump of the spontaneous strain with increasing x.

The predictions for the temperature-dependence of the effective elastic constant (see Ref. [6] for definition) useful for the future thermoelastic study is shown in Figure 8. An interesting feature of Figure 8 is that the softening of the elastic constant does not point zero whenever the metastable phase exists in the whole temperature range.

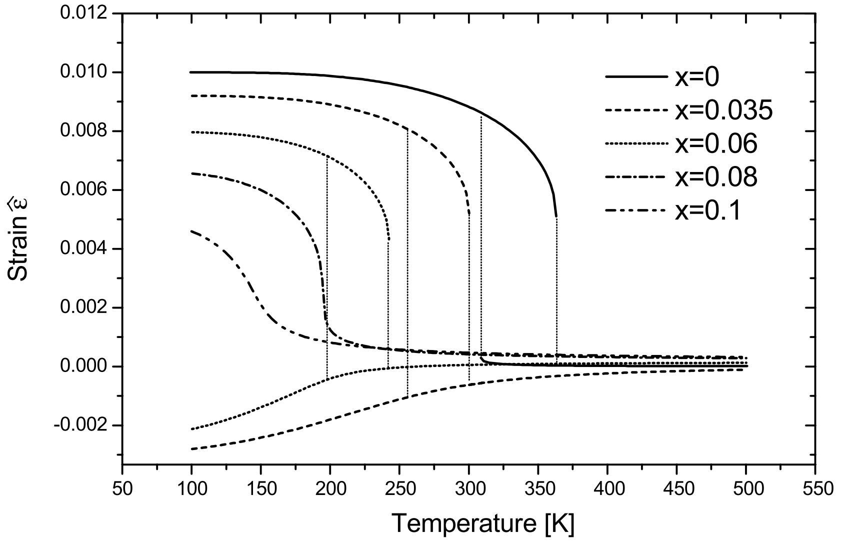

Fig. 6. Spontaneous strain (Eq. (30)) evaluated for the parameters of Figure 4.

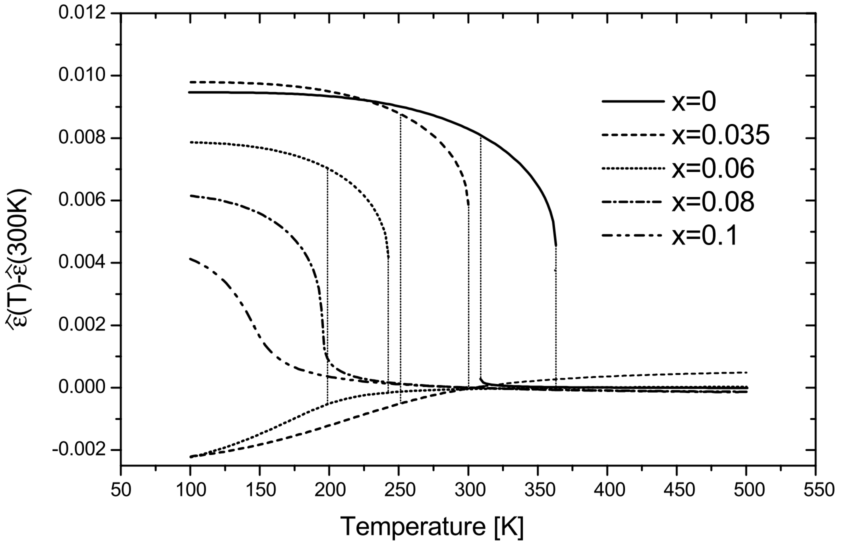

Fig. 7. Curves from Figure 6 adjusted to $T = 300$ K for direct comparison with experiment (Ref. [8]).

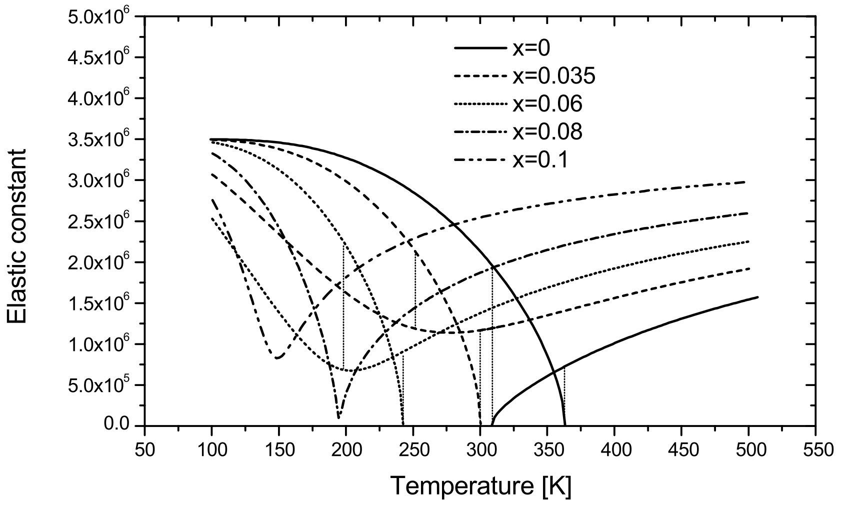

Fig. 8. Thermoelastic behaviour of elastic constant (Eq. (3) or λ_- of Eq. (A.1)) as predicted by pseudospin model.

4 Discussion

The anisotropic pseudospin model presented in Section 3 relates the first order phase transition hcp-2→hcp-1 in $C_{70(1-x)}C_{60x}$ to the 'entropic' field $h_{\mathrm{s}} = -k_{\mathrm{B}}T\ln(3)/2$ due to the higher multiplicity of the state with $s \approx -1$ in the Ising Hamiltonian of equation (13). The mechanism of this phase transition is, therefore, substantially different from that implied by a strong enough coupling of the orientational order parameter with strain [6,7]. The increase in the amount x of the C_{60} molecules apparently drives the system $C_{70(1-x)}C_{60x}$ towards the critical point. Typical Landau theory would then require a strengthening of the local quadrupolar field with the dilution x (see Eq. (4) and Ref. [19]). However, an admixture of more spherical C_{60} should rather weaken this field. The field $\hat{h}$ resulting from the pseudospin model does really weaken with x (see Eq. (34)) as a consequence of the temperature-dependent field h_{s} (Eq. (24)).

Two experimental observations, which could have been thought of as artefacts find a clear explanation in the present model. Firstly, a dip in the temperature dependence of the strain near the phase transition [8] is easily visible for $x = 0.035$ and $x = 0.06$ in Figure 6. Secondly, the x-dependence of the jump of the strain at the phase transition showing an initial increase followed by a decrease with increasing x can be identified in Figure 7.

Doubts can be raised, however, about the behaviour of the system for the concentrations x close to $x \approx 0.08$. The assumption of the critical point at $x \approx 0.088$ implies that both the width of the hysteresis and the jump of the strain should tend to zero by approaching this point. The parameters of equations (34) allow one to keep the width of the hysteresis fairly large down to quite close to the critical point in accordance with the experimental observations. The corresponding jump of the strain rests, however, also large in this range of concentration x, whereas it shows a significant decrease in experiment (*e.g.* compare the jump of strain at $x = 0.06$, Figure 7, and the corresponding curve of Ref. [8]). The existence of the metastable phase with negative order parameter $\bar{s}$ suggests a kinetic origin of this discrepancy. Namely, the prediction exhibited in Figures 4–8 concern an idealized experiment with the cooling rate tending to zero, whereas the experimental cooling rate always differs from zero. Therefore, an amount of the sample rests in the initial disordered metastable phase. This amount should increase with increasing cooling rate and with decreasing transition temperature. The actual critical point then would follow from the limit of the infinitely slow cooling. A series of experiments with different cooling rates are feasible with the DMA apparatus and will be done in future. At the present stage we can estimate the fraction γ of the disordered phase subsisting below the phase transition by comparison of the theoretical "quasistatic" jumps of the strain of Figure 7 with the experimental ones. Thus, $\gamma \approx 0$, at $x = 0$ and $x = 0.35$, $\gamma \approx 43\%$ at $x = 0.05$ and $\gamma \approx 83\%$, at $x = 0.06$. It would be interesting to compare these estimates with spectroscopic observations of molecular motions (see Ref. [21] for an example of similar studies in the fcc structure).

All the above considerations describe the orientational ordering of the C_{70} molecules in the mixed system $C_{70(1-x)}C_{60x}$ as an interplay between the ordered phase with $s \approx 1$ and the disordered phase with $s \approx -1$ where the pseudospin states ②, ③ and ④ (Fig. 1) are occupied with equal probability. We have shown that this effect dominates over the influence of the random fields and random bonds, which only accelerates the approach to the critical point.

An intriguing question is the physical reason for a tremendously strong dependence of the model parameters on the concentration x (see Eq. (34)). The mechanism of this dependence seems to be similar to that observed in granular media, where the introduction of a steric impurity creates a system of defects extending to a very long distance [26].

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Appendix A

There are two independent normal strains and two corresponding elastic parameters of symmetry A_1' in the hexagonal media. The elastic parameters are

$$\lambda_{\pm} = \frac{1}{2}\Bigg\{(c_{11}+c_{12}+c_{33}) \pm\sqrt{(c_{11}+c_{12}+c_{33})^2 - 4\left[(c_{11}+c_{12})c_{33} - 2c_{13}^2\right]}\Bigg\}, \tag{A.1}$$

whereas the normal strain have a general form $(\varepsilon_{11}, \varepsilon_{22}, \varepsilon_{33}) = (\alpha, \alpha, \beta)$ with

$$\frac{\alpha_{\pm}}{\beta_{\pm}} = \frac{(\lambda_{\pm} - c_{33})}{2c_{13}}. \tag{A.2}$$

The soft elastic parameter at the critical point of the isomorphous phase transition is the lower of the values of equation (A.1).

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