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► **To cite this version:**

| Jamil A Nasser. A microscopic model for the phase diagramm of a pur substance. 2021. hal-03373139

**HAL Id: hal-03373139**

**<https://hal.uvsq.fr/hal-03373139>**

Preprint submitted on 11 Oct 2021

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# A microscopic model for the phase diagramm of a pur substance

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October 9, 2021

## Abstract

Recently, a two-dimensional model that leads to first order phase transitions has been proposed. This model also leads to phase diagrams which present the characteristics observed in phase diagrams of the substances : three thermodynamic phases, three coexistence curves, a triple point and a critical point.

In the present study, the calculation of the latent heats of the different first order phase transitions as well as the experimental data concerning the phase diagram of a pure substance, here carbon dioxyde, are introduced into the two-dimensional model.

By assuming that the pressure does not modify the chemical bond between two nearest-neighbors atoms but modifies that between two next nearest-neighbors atoms we can calculated the phase diagram of the compound in  $(bar, Kelvin)$  plane and the *Joule* values of the different latent heats of transition. Moreover, the energy value of the chemical bond between two nearest-atoms is obtained.

## 1 Introduction

Let us consider a cristal of  $N$  identical atoms. In the adiabatic approximation, it can be considered as a set of electronic bonds ( or chemical bonds) and elastic springs between the atoms, each elastic spring being related to a bond [1 – 2]. So any modification of the quantum states of the electrons involved in a chemical bond can modify the elastic force constant of the spring associated to it. We consider harmonic vibrations.

Recently [3], a two-dimensional model taking into account this kind of atoms-phonon coupling leads to a phase diagram which displays, at least qualitatively, the features observed in the phase diagram of a pure substance: first order phase transitions between three thermodynamic phases, three coexistence curves, one triple point and one critical point. In this model it is assumed that, for each atom, the electrons involved in the bond between this atom and its nearest-neighbors are different from those involved in the bond between this atom and its next nearest-neighbors. It is assumed that each kind of electrons has two energy levels. These assumptions lead to a coupling between a chemical bond and the spring associated to it. This coupling is described below.

Let us consider the bond between two atoms nearest neighbors. The potential energy between those atoms can have three values depending on the quantum states of electrons involved in the bond. Let us call  $V_0(r)$  this potential energy when the electrons of both atoms are in their fundamental level, where  $r$  is the distance between both atoms. It is assumed that  $V_0(r)$  has a minimum for  $r = r_0$  and a second derivative equal to  $\lambda$  at the minimum. Let us call  $V_1(r)$  this potential energy when the electrons of both atoms are in their excited level. It is assumed that  $V_1(r)$  has a minimum for  $r = r_1$  and a second derivative equal to  $\nu$  at the minimum. We neglect the difference between  $r_0$  and  $r_1$  and we assume that  $\nu$  is smaller than  $\lambda$ . As  $\nu < \lambda$ , the vibrational energy of both atoms is smaller when the electrons are in their excited level than when they are in their fundamental level. Consequently, when the electrons are in their fundamental level the electronic energy is small but the vibrational energy is large, while, when they are in their excited level, the electronic energy is large but the vibrational energy is small. So there is a competition between the electronic interactions which favour the fundamental levels and the vibration interactions which favour the excited one. This competition can lead to a first order phase transition [4].

In the present study we add to the two-dimensional model the calculation of the latent heats of the different first order phase transitions. Moreover, using the experimental data concerning the phase diagram of the carbon dioxide,  $CO_2$ , we show how those data can be introduced in the model and which results can be obtained. In Section 2, we present the crystal Hamiltonian and the method used to study it. In Section 3 we give the results obtained by the numerical study, and the last Section is devoted to discussion and conclusion.

## 2 Theoretical study

### 2.1 Lattice Hamiltonian

Let us consider a square lattice of  $N$  identical atoms. Each atom  $l$  moves around a lattice point  $l$ . The position vector of the lattice point  $l$  is

$$\vec{R}_l = l_1 \vec{a}_1 + l_2 \vec{a}_2 \quad (1)$$

where  $\vec{a}_1$  and  $\vec{a}_2$ , the basis vectors of the lattice, are orthogonal and have the same length  $a_0$ , and where  $l_1 = 0, 1, 2, \dots, N_1 - 1$  and  $l_2 = 0, 1, 2, \dots, N_2 - 1$ . So the lattice point  $l$  is defined by the set  $(l_1, l_2)$ , and we can write  $l = (l_1, l_2)$ . It is clear that  $N = N_1 N_2$ .

For studying the atoms movements, we introduce the orthogonal axes  $\vec{Ox}$  and  $\vec{Oy}$  which are parallel to  $\vec{a}_1$  and  $\vec{a}_2$ , respectively, the origin,  $O$ , being at the lattice point  $(0, 0)$ . We assume that each atom is linked to its four nearest neighbors and to its four next-nearest neighbors by harmonic springs.

The four nearest neighbors of the atom  $l = (l_1, l_2)$ , are the atoms :  $l^{(1)} = (l_1 + 1, l_2)$ ,  $l^{(2)} = (l_1, l_2 + 1)$ ,  $l^{(3)} = (l_1 - 1, l_2)$  and  $l^{(4)} = (l_1, l_2 - 1)$ . We call  $e_{ll^{(\alpha)}}$ , the elastic force constant of the spring linking the atoms  $l$  and  $l^{(\alpha)}$ , with  $\alpha = 1, 2, 3, 4$ . The potential energy of the elastic interaction between the atom  $l$  and its four nearest neighbors is  $E_{p1}(l)$  given by

$$E_{p1}(l) = \frac{1}{2} (e_{ll^{(1)}} (u_l - u_{l^{(1)}})^2 + e_{ll^{(3)}} (u_l - u_{l^{(3)}})^2 + e_{ll^{(2)}} (v_l - v_{l^{(2)}})^2 + e_{ll^{(4)}} (v_l - v_{l^{(4)}})^2) \quad (2)$$

where  $u_l$  and  $v_l$  are the components, on the respective axes  $\vec{Ox}$  and  $\vec{Oy}$ , of the displacement of the atom  $l$  around the lattice point  $l$ . So, the total elastic interaction between pairs of atoms nearest neighbors is

$$E_{p1tot} = \frac{1}{2} \sum_{(l)} E_{p1}(l) \quad (3)$$

$\sum_{(l)}$  is the sum over the  $N$  lattice points. Periodic boundary conditions are assumed.

The four next-nearest neighbors of the atom  $l = (l_1, l_2)$  are the atoms:  $L^{(1)} = (l_1 + 1, l_2 + 1)$ ,  $L^{(2)} = (l_1 - 1, l_2 + 1)$ ,  $L^{(3)} = (l_1 - 1, l_2 - 1)$  and  $L^{(4)} = (l_1 + 1, l_2 - 1)$ . We call  $\tilde{e}_{l,L^{(\alpha)}}$ , the elastic force constant of the spring which links the atoms  $l$  and  $L^{(\alpha)}$ , with  $\alpha = 1, 2, 3, 4$ . The potential energy of the elastic interaction between the atom  $l$  and its four next- nearest neighbors is

$$E_{p2}(l) = \frac{1}{2} (\tilde{e}_{lL(1)} b_{lL(1)} + \tilde{e}_{lL(2)} b_{lL(2)} + \tilde{e}_{lL(3)} b_{lL(3)} + \tilde{e}_{lL(4)} b_{lL(4)}) \quad (4)$$

with

$$b_{lL(1)} = \frac{1}{2} (u_{L(1)} - u_l + v_{L(1)} - v_l)^2 \quad (5)$$

$$b_{lL(2)} = \frac{1}{2} (u_l - u_{L(2)} + v_{L(2)} - v_l)^2 \quad (6)$$

$$b_{lL(3)} = \frac{1}{2} (u_{L(3)} - u_l + v_{L(3)} - v_l)^2 \quad (7)$$

$$b_{lL(4)} = \frac{1}{2} (u_l - u_{L(4)} + v_{L(4)} - v_l)^2 \quad (8)$$

So, the total elastic interaction between pairs of atoms next-nearest neighbors is

$$E_{p2tot} = \frac{1}{2} \sum_{(l)} E_{p2}(l) \quad (9)$$

The Hamiltonian of the crystal vibrations is

$$H_{ph} = E_c + E_{p1tot} + E_{p2tot} \quad (10)$$

where  $E_c$  is the kinetic energy of the atoms.

Now we introduce the following assumptions :

i) Each atom  $l$  contains two electronic subsystems (1) and (2). The electronic subsystem (1) contains the electrons which are involved in the bond between the atom  $l$  and its four nearest neighbors and the electronic subsystem (2) contains the electrons which are involved in the bond between the atom  $l$  and its four next-nearest neighbors. The electronic subsystem ( $i$ ) ( $i = 1, 2$ ) has two energy levels separated by  $\Delta_i$ : the fundamental level, called ( $a_i$ ) is not degenerated while the excited one, called ( $b_i$ ) has the degeneracy  $r_i$ . To the subsystem ( $i$ ) is associated the fictitious spin  $\hat{\sigma}_{il}$  which has two eigenvalues  $\sigma_{il} = \pm 1$ . In others words, each subsystem ( $i$ ) has its own space of quantum states and its physical observable  $\hat{\sigma}_{il}$ . And we work in the tensorial ( or direct) product of both spaces.

The electronic Hamiltonian of the atom  $l$  can be written

$$H_e(l) = \frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \quad (11)$$

and the electronic Hamiltonian of the crystal is

$$H_e = \sum_{(l)} \left( \frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \right) \quad (12)$$

ii) The value of the spring constant  $e_{ll^{(\alpha)}}$ , with  $\alpha = 1, \dots, 4$ , depends only on the quantum states of the electronic subsystems (1) of the atoms  $l$  and  $l^{(\alpha)}$  following the relation

$$e_{ll^{(\alpha)}} = \frac{\lambda + 2\mu + \nu}{4} + \frac{\nu - \lambda}{4} (\sigma_{1l} + \sigma_{1l^{(\alpha)}}) + \frac{\lambda - 2\mu + \nu}{4} \sigma_{1l} \sigma_{1l^{(\alpha)}} \quad (13)$$

We can verify that the above formula gives  $e_{ll^{(\alpha)}} = \lambda$  when  $\sigma_{1l} = \sigma_{1l^{(\alpha)}} = -1$ ,  $e_{ll^{(\alpha)}} = \nu$  when  $\sigma_{1l} = \sigma_{1l^{(\alpha)}} = +1$  and  $e_{ll^{(\alpha)}} = \mu$  when  $\sigma_{1l} \neq \sigma_{1l^{(\alpha)}}$ . Moreover, we assume that

$$\lambda \geq \mu \geq \nu \quad (14)$$

iii) The value of the spring constant  $\tilde{e}_{lL^{(\alpha)}}$ , with  $\alpha = 1, \dots, 4$ , depends only on the quantum states of the electronic subsystems (2) of the atoms  $l$  and  $L^{(\alpha)}$  following the relation

$$\tilde{e}_{lL^{(\alpha)}} = \frac{\tilde{\lambda} + 2\tilde{\mu} + \tilde{\nu}}{4} + \frac{\tilde{\nu} - \tilde{\lambda}}{4} (\sigma_{2l} + \sigma_{2L^{(\alpha)}}) + \frac{\tilde{\lambda} - 2\tilde{\mu} + \tilde{\nu}}{4} \sigma_{2l} \sigma_{2L^{(\alpha)}} \quad (15)$$

We can verify that the above formula gives  $\tilde{e}_{lL^{(\alpha)}} = \tilde{\lambda}$  when  $\sigma_{2l} = \sigma_{2L^{(\alpha)}} = -1$ ,  $\tilde{e}_{lL^{(\alpha)}} = \tilde{\nu}$  when  $\sigma_{2l} = \sigma_{2L^{(\alpha)}} = +1$  and  $\tilde{e}_{lL^{(\alpha)}} = \tilde{\mu}$  when  $\sigma_{2l} \neq \sigma_{2L^{(\alpha)}}$ . Moreover, we assume that

$$\tilde{\lambda} \geq \tilde{\mu} \geq \tilde{\nu} \quad (16)$$

The Hamiltonian of the crystal,  $H$ , is the sum of  $H_{ph}$  and  $H_e$ . So,

$$H = E_c + E_{p1tot} + E_{p2tot} + \sum_{(l)} \left( \frac{\Delta_1}{2} \hat{\sigma}_{1l} + \frac{\Delta_2}{2} \hat{\sigma}_{2l} \right) \quad (17)$$

## 2.2 Reduced parameters

It is interesting to take  $\lambda$  and  $\tilde{\lambda}$  as the units of elastic force constant and to introduce the sets of reduced parameters  $(x, y)$  and  $(\tilde{x}, \tilde{y})$  defined by

$$x = \frac{\nu}{\lambda} \quad (18)$$

$$\tilde{x} = \frac{\tilde{\nu}}{\tilde{\lambda}} \quad (19)$$

$$2\mu = (\lambda + \nu) + y(\lambda - \nu) \quad (20)$$

$$2\tilde{\mu} = (\tilde{\lambda} + \tilde{\nu}) + \tilde{y}(\tilde{\lambda} - \tilde{\nu}) \quad (21)$$

From the relations (14) and (16), the parameters  $x$  and  $\tilde{x}$  are comprised between 0 and 1, and the parameters  $y$  and  $\tilde{y}$  must be comprised between  $-1$  and  $+1$ .

With these new parameters,  $e_{ll(\alpha)}$  and  $\tilde{e}_{lL(\alpha)}$  can be written

$$e_{ll(\alpha)} = \lambda(a + b(\sigma_{1l} + \sigma_{1l(\alpha)}) + c \sigma_{1l}\sigma_{1l(\alpha)}) \quad (22)$$

and

$$\tilde{e}_{lL(\alpha)} = \tilde{\lambda}(\tilde{a} + \tilde{b}(\sigma_{2l} + \sigma_{2L(\alpha)}) + \tilde{c} \sigma_{2l}\sigma_{2L(\alpha)}) \quad (23)$$

with

$$a = \frac{1+x}{2} - c \quad (24)$$

$$b = \frac{x-1}{4} \quad (25)$$

$$c = yb \quad (26)$$

and

$$\tilde{a} = \frac{1+\tilde{x}}{2} - \tilde{c} \quad (27)$$

$$\tilde{b} = \frac{\tilde{x}-1}{4} \quad (28)$$

$$\tilde{c} = \tilde{y}\tilde{b} \quad (29)$$

It is worth to notice that the parameters  $b$  and  $\tilde{b}$  are negative or equal to zero.

### 2.3 Phonon - atom interaction

By inserting relation (22) in the expression of  $E_{p1}(l)$ , equation (2), the potential energy  $E_{p1tot}$  can be written

$$E_{p1tot} = \frac{1}{4}\lambda a \sum_{(l)} A_l + V_Z + V_{Ex} \quad (30)$$

with

$$A_l = (u_l - u_{l(1)})^2 + (u_l - u_{l(3)})^2 + (v_l - v_{l(2)})^2 + (v_l - v_{l(4)})^2 \quad (31)$$

$$V_Z = \frac{1}{2}\lambda b \sum_{(l)} A_l \sigma_{1l} \quad (32)$$

and

$$\begin{aligned} V_{Ex} = & \frac{1}{2}\lambda c \sum ((u_l - u_{l(1)})^2 \sigma_{1l}\sigma_{1l(1)} + (u_l - u_{l(3)})^2 \sigma_{1l}\sigma_{1l(3)} \\ & + (v_l - v_{l(2)})^2 \sigma_{1l}\sigma_{1l(2)} + (v_l - v_{l(4)})^2 \sigma_{1l}\sigma_{1l(4)}) \end{aligned} \quad (33)$$

The energy term  $V_Z$  is a Zeeman-like interaction which can be written

$$V_Z = \sum_{(l)} -h_l \hat{\sigma}_{1l} \quad (34)$$

with

$$h_l = -\frac{1}{2} \lambda b A_l \quad (35)$$

As the parameter  $b$  is negative, the field-like  $h_l$  which acts on the fictitious spins  $\hat{\sigma}_{1l}$  favours the eigen value  $\sigma_{1l} = +1$ .

The energy term  $V_{Ex}$  is an exchange-like interaction between the fictitious spin  $\hat{\sigma}_{1l}$  and its four nearest neighbors  $\hat{\sigma}_{1l^{(\alpha)}}$  ( $\alpha = 1, \dots, 4$ ). When the parameter  $c$  is positive, this interaction favours the case  $\sigma_{1l} = -\sigma_{1l^{(\alpha)}}$  when this parameter is negative this interaction favours the case  $\sigma_{1l} = \sigma_{1l^{(\alpha)}}$  and when it is equal to zero, the exchange-like interaction is equal to zero.

For the following we assume

$$y = 0 \quad (36)$$

which implies that the exchange-like interaction  $V_{Ex}$  is equal to zero.

By inserting relation (23) in the expression of  $E_{p2}(l)$ , equation (4), the potential energy  $E_{p2tot}$  can be written

$$E_{p2tot} = \frac{1}{4} \tilde{\lambda} \tilde{a} \sum_{(l)} B_l + \tilde{V}_Z + \tilde{V}_{Ex} \quad (37)$$

with

$$B_l = b_{lL^{(1)}} + b_{lL^{(2)}} + b_{lL^{(3)}} + b_{lL^{(4)}} \quad (38)$$

$$\tilde{V}_Z = \frac{1}{2} \tilde{\lambda} \tilde{b} \sum_{(l)} B_l \hat{\sigma}_{2l} \quad (39)$$

and

$$\tilde{V}_{Ex} = \frac{\tilde{\lambda} \tilde{c}}{2} \sum_{(l)} (b_{lL^{(1)}} \sigma_{2l} \sigma_{2L^{(1)}} + b_{lL^{(2)}} \sigma_{2l} \sigma_{2L^{(2)}} + b_{lL^{(3)}} \sigma_{2l} \sigma_{2L^{(3)}} + b_{lL^{(4)}} \sigma_{2l} \sigma_{2L^{(4)}}) \quad (40)$$

As previously, the energy term  $\tilde{V}_Z$  is a Zeeman-like interaction. As the parameter  $\tilde{b}$  is negative, the field-like which acts on the fictitious spin  $\hat{\sigma}_{2l}$  favours the eigenvalue  $\sigma_{2l} = +1$ . The energy term  $\tilde{V}_{Ex}$  is an exchange-like interaction between the fictitious spin  $\hat{\sigma}_{2l}$  and its next-nearest neighbors  $\hat{\sigma}_{2L^{(\alpha)}}$  ( $\alpha = 1, \dots, 4$ ).



When the parameter  $\tilde{c}$  is positive, this interaction favours the case  $\sigma_{2l} = -\sigma_{2L(\alpha)}$  when this parameter is negative this interaction favours the case  $\sigma_{2l} = \sigma_{1L(\alpha)}$  and when it is equal to zero, the exchange-like interaction is equal to zero.

For the following we assume that

$$\tilde{y} = 0 \quad (41)$$

which implies that the exchange-like interaction  $\tilde{V}_{Ex}$  is equal to zero.

## 2.4 Variational method: effective parameters

For the variational Hamiltonian  $H_0$  [5, 6], we take the sum of a phonon Hamiltonian  $H_{0ph}$  and a spin Hamiltonian  $H_{0sp}$

$$H_0 = H_{0ph} + H_{0sp} \quad (42)$$

### 2.4.1 Variational phonon Hamiltonian $H_{0ph}$

We introduce two parameters  $E$  and  $\tilde{E}$ . The first one,  $E$ , is an effective spring constant that replaces the spring constants  $e_{l(\alpha)}$ , and the second one,  $\tilde{E}$ , is an effective spring constant that replaces the spring constants  $\tilde{e}_{lL(\alpha)}$ . Those  $E$  and  $\tilde{E}$  do not depend on the electronic states of the subsystems (1) and (2). The phonon Hamiltonian  $H_{0ph}(E, \tilde{E})$  is then

$$H_{0ph}(E, \tilde{E}) = E_c + E_{p10}(E) + E_{p20}(\tilde{E}) \quad (43)$$

with

$$E_{p10}(E) = \frac{1}{2} \sum_{(l)} \frac{1}{2} E A_l \quad (44)$$

$$E_{p20}(\tilde{E}) = \frac{1}{2} \sum_{(l)} \frac{1}{2} \tilde{E} B_l \quad (45)$$

The Hamiltonian  $H_{0ph}(E, \tilde{E})$  is the Hamiltonian of vibrations of a square lattice of atoms linked by springs between atoms nearest neighbors and atoms next-nearest neighbors with the spring constants  $E$  and  $\tilde{E}$ , respectively. It is known that there are two dispersion relations

$$\omega = \omega_1(\vec{k})$$

and

$$\omega = \omega_2 \left( \vec{k} \right)$$

which correspond to two acoustic branches of the crystal. In the previous relations the vector  $\vec{k}$  is the phonons wave vector. The previous dispersion relations are in agreement with those obtained by Blackman [7] and de Launay [8]. They are given in the Appendix.

The free energy associated to the Hamiltonian  $H_{0ph} \left( E, \tilde{E} \right)$  is

$$F_{0ph} = k_B T \sum'_{\left( \vec{k} \right)} \ln \left( 2 \sinh \left( \beta \frac{\hbar \omega \left( \vec{k} \right)}{2} \right) \right) \quad (46)$$

where  $k_B$  is the Boltzmann constant,  $\beta = \frac{1}{k_B T}$  and  $\sum'_{\left( \vec{k} \right)}$  is the sum over the

two phonons branches. Using the matrix density of  $H_{0ph} \left( E, \tilde{E} \right)$ , the thermal mean values  $\langle A_l \rangle_0$  and  $\langle B_l \rangle_0$  of the parameters  $A_l$  and  $B_l$ , respectively, are

$$\langle A_l \rangle_0 = \frac{4}{N} \sum'_{\left( \vec{k} \right)} \coth \left( \beta \frac{\hbar \omega \left( \vec{k} \right)}{2} \right) \frac{\hbar}{2} \frac{\partial \omega}{\partial E} \quad (47)$$

and

$$\langle B_l \rangle_0 = \frac{4}{N} \sum'_{\left( \vec{k} \right)} \coth \left( \beta \frac{\hbar \omega \left( \vec{k} \right)}{2} \right) \frac{\hbar}{2} \frac{\partial \omega}{\partial \tilde{E}} \quad (48)$$

where  $\frac{\partial \omega}{\partial E}$  and  $\frac{\partial \omega}{\partial \tilde{E}}$  are the partial derivatives of the dispersion relations. The expressions of  $\frac{\partial \omega}{\partial E}$  and  $\frac{\partial \omega}{\partial \tilde{E}}$  are given in the Appendix.

#### 2.4.2 Variational spin Hamiltonian $H_{0sp}$

We consider the case where the exchange-like interactions  $V_{Ex}$  and  $\tilde{V}_{Ex}$  are equal to zero. We introduce two fields-like  $h_1$  and  $h_2$  which act over the fictitious spin  $\hat{\sigma}_{1l}$  and  $\hat{\sigma}_{2l}$ , respectively. Those fields-like are uniform.

The spin Hamiltonian  $H_{0sp}$  is

$$H_{0sp} = H_{0sp1} + H_{0sp2} \quad (49)$$

with

$$H_{0sp1} = \sum_{(l)} -h_1 \hat{\sigma}_{1l} \quad (50)$$

and

$$H_{0sp2} = \sum_{(l)} -h_2 \hat{\sigma}_{2l} \quad (51)$$

With this spin Hamiltonians, all the fictitious spins of the electronic subsystem  $i$ , ( $i = 1, 2$ ), have the same thermal mean value  $m_i$  given by

$$m_i = \frac{-\exp(-\beta h_i) + r_i \exp(\beta h_i)}{\exp(-\beta h_i) + r_i \exp(\beta h_i)} \quad (52)$$

The equations (52) are called self-consistent equations.

The free energy related to  $H_{0sp}$  is

$$F_{0sp} = -Nk_B T (\ln z_{0sp1} + \ln z_{0sp2}) \quad (53)$$

where the partition function  $z_{0spi}$  is given by

$$z_{0spi} = \exp(-\beta h_i) + r_i \exp(\beta h_i) \quad (54)$$

### 2.4.3 Variational Hamiltonian $H_0$

So, the variational Hamiltonian is given by

$$H_0 = E_c + E_{p10}(E) + E_{p20}(\tilde{E}) + \sum_{(l)} -h_1 \hat{\sigma}_{1l} + \sum_{(l)} -h_2 \hat{\sigma}_{2l} \quad (55)$$

The free energy associated with  $H_0$  is given by

$$F_0 = F_{0ph} + F_{0sp} \quad (56)$$

that is

$$F_0 = k_B T \sum_{(\vec{k})}' \ln \left( 2 \sinh \left( \beta \frac{\hbar \omega(\vec{k})}{2} \right) \right) - Nk_B T \ln z_{0sp1} - Nk_B T \ln z_{0sp2} \quad (57)$$

### 2.4.4 Thermodynamic parameters

At the first order of a perturbation calculation we obtain the following results.

$$E = \lambda (a + 2bm_1 + cm_1^2) \quad (58)$$

$$\tilde{E} = \tilde{\lambda} (\tilde{a} + 2\tilde{b}m_2 + \tilde{c}m_2^2) \quad (59)$$

$$h_1 = -\frac{\Delta_1}{2} - \frac{1}{2} \langle A_l \rangle_0 \lambda (b + cm_1) \quad (60)$$

$$h_2 = -\frac{\Delta_2}{2} - \frac{1}{2} \langle B_l \rangle_0 \tilde{\lambda} (\tilde{b} + \tilde{c}m_2) \quad (61)$$

In the present study the parameters  $c$  and  $\tilde{c}$  are equal to zero. The crystal free energy, at the thermodynamic equilibrium, is

$$F = F_0 + N \left( \frac{\Delta_1}{2} + h_1 \right) m_1 + N \left( \frac{\Delta_2}{2} + h_2 \right) m_2 \quad (62)$$

The fraction of atoms in the excited level ( $b_1$ ) is

$$n_1 = \frac{1 + m_1}{2} \quad (63)$$

and the fraction of atoms in the excited level ( $b_2$ ) is

$$n_2 = \frac{1 + m_2}{2} \quad (64)$$

When the parameter  $m_i$  ( $i = 1, 2$ ) is equal to  $-1$ , the fraction  $n_i$  is equal to zero and the electronic subsystems ( $i$ ) are in the fundamental level ( $a_i$ ) and when  $m_i = +1$ , they are in the excited level ( $b_i$ ).

We can calculate the crystal entropy by using the relation

$$S = -\frac{\partial F}{\partial T} \quad (65)$$

So we obtain

$$S = S_{ph} + S_{sp} \quad (66)$$

with

$$S_{ph} = \frac{1}{T} \sum'_{(\vec{k})} \coth \left( \beta \frac{\hbar\omega(\vec{k})}{2} \right) \frac{\hbar\omega(\vec{k})}{2} - k_B \sum'_{(\vec{k})} \ln \left( 2 \sinh \left( \beta \frac{\hbar\omega(\vec{k})}{2} \right) \right) \quad (67)$$

and

$$S_{sp} = Nk_B (\ln z_{0sp1} + \ln z_{0sp2}) - N \frac{1}{T} (m_1 h_1 + m_2 h_2) \quad (68)$$

From the relation

$$F = U - TS \quad (69)$$

we deduce for the internal energy  $U$

$$U = \sum'_{(\vec{k})} \coth \left( \beta \frac{\hbar\omega(\vec{k})}{2} \right) \frac{\hbar\omega(\vec{k})}{2} + N \frac{\Delta_1}{2} m_1 + N \frac{\Delta_2}{2} m_2 \quad (70)$$

We recall that in a first order phase transition there is not a discontinuity in  $F$ , but there are a discontinuity in the extensive parameters  $Nn_1$ ,  $Nn_2$ ,  $S$ , and  $U$ . At the transition,  $\Delta S$ , the discontinuity in  $S$ , and  $\Delta U$ , the discontinuity in  $U$ , are related by

$$\Delta U = T \Delta S \quad (71)$$

where  $T$  is the transition temperature. The latent heat of the transition  $L$  is given by

$$L = T \Delta S = \Delta U \quad (72)$$

### 3 Numerical study

The numerical study consists essentially in solving the self-consistent equations (52) by taking into account the relations (58) to (61). Both self-consistent equations are coupled.

#### 3.1 New reduced parameters

It is interesting to introduce new reduced parameters by taking  $\hbar\omega_M(\lambda)$  as the unit of energy with

$$\omega_M(\lambda) = 2\sqrt{\frac{\lambda}{m_a}} \quad (73)$$

where  $m_a$  is the mass of the atoms. The value of  $\hbar\omega_M(\lambda)$  is roughly estimated to  $1000K$  or  $695 \text{ cm}^{-1}$ .

With this unit of energy, we introduce the following reduced parameters:

- the reduced temperature

$$t = \frac{k_B T}{\hbar\omega_M(\lambda)} \quad (74)$$

- the reduced energy gaps

$$\delta_1 = \frac{\Delta_1}{\hbar\omega_M(\lambda)} \quad (75)$$

and

$$\delta_2 = \frac{\Delta_2}{\hbar\omega_M(\lambda)} \quad (76)$$

- the reduced free energy per atom that we call reduced free energy

$$f = \frac{1}{N\hbar\omega_M(\lambda)}F \quad (77)$$

- the reduced internal energie per atom that we call reduced internal energy

$$u = \frac{U}{N\hbar\omega_M(\lambda)} \quad (78)$$

The quantities  $t$ ,  $\delta_1$ ,  $\delta_2$ ,  $f$  and  $u$  have no unit.

- We call reduced entropy, which is denoted  $s$ , the entropy per atom in the unit  $k_B$  ( Boltzmann constant). So,

$$s = \frac{1}{k_B} \frac{S}{N} \quad (79)$$

The quantity  $s$  has no unit.

From (79), a variation of  $s$ ,  $\Delta s$ , is related to an entropy variation,  $\Delta S$ , by the relation

$$\Delta s = \frac{1}{k_B} \frac{\Delta S}{N} \quad (80)$$

Using the definition of the reduced temperature  $t$ , we have

$$t\Delta s = \frac{T\Delta S}{N\hbar\omega_M(\lambda)} \quad (81)$$

In a first order transition  $T\Delta S$  is the latent of the transition,  $\Delta S$  being the discontinuity in entropy at the transition. Then,  $t\Delta s$  is the reduced latent heat per atom at the transition that we call reduced latent heat.

We can caculate  $f$ ,  $u$  and  $s$ .

### 3.2 Study of the self-consistent equations

We fix the values of the temperature and that of all the model parameters and we look for the values of  $m_1$  and  $m_2$  which satisfy the self-consistent equations (52). A solution is a set  $(m_1, m_2)$  or  $(n_1, n_2)$ . For each solution we can calculate the values of the thermodynamic parameters  $f$ ,  $u$  and  $s$ .

If there is one solution, this solution is the stable solution ( or the stable state or the thermodynamic state of the crystal). If there are several solutions, the reduced free energy values of those solutions must be compared. The solution which has the lowest reduced free energy value is the stable state. When the reduced free energy values of two solutions  $(n_1, n_2)$  and  $(n'_1, n'_2)$  are equal and

are the lowest, both solutions are the thermodynamic states of the crystal which then displays a first order phase transition between those thermodynamic states.

At the transition, the parameters  $Nn_i$  ( $i = 1, 2$ ), the crystal entropy and the internal energy display a discontinuity. In some cases, the magnitude of those discontinuities decrease when the transition temperature increases and are equal to zero when the temperature is higher or equal to a temperature value  $T_C$  ( or  $t_C$ ). We have used this property for finding  $t_C$ . The value  $t_C$  is called reduced critical temperature.

It is worth to count the number of independent parameters. In this study  $N_1 = 40$ ,  $N_2 = 50$ ,  $r_1 = r_2 = 4$ ,  $y = \tilde{y} = 0$ ,  $z = \tilde{\lambda} = 0.2$ ,  $\delta_1 = 10$  and  $x = 10^{-5}$ . So, a thermodynamic state of the system, that is a stable solution, depends on the three parameters :  $\delta_2$ ,  $\tilde{x}$  and  $t$ . A first order phase transition implies the existence of one relation between those parameters and a triple point implies the existence of another relation between those parameters. So, at the phase transition, the transition temperature, the magnitude of the discontinuities and the latent heat values depend on the two parameters  $\delta_2$  and  $\tilde{x}$ . At a triple point, the triple point temperature, the magnitude of the discontinuities and the latent heats values, depend on one parameter  $\tilde{x}$  or  $\delta_2$ . We take  $\tilde{x}$  as the independent parameter.

One can expect that the stable state is (0.000, 0.000) at very low temperature and (1., 1.) at high temperature. Between the brackets, the first number corresponds to the value of  $n_1$  and the second one to that of  $n_2$ .

### 3.3 Phase diagram for $\tilde{x}$ constant

#### 3.3.1 Phases and discontinuities

A phase diagram of the crystal in the  $(\delta_2, t)$  plane for  $\tilde{x} = 0.0263$  is shown in Fig.1. The coordinates of the point  $T$  are  $(\delta_{2T} = 14.84919, t_T = 3.032334)$ . The method for obtaning those coordinates is explained in [3] and in the following.

When the value of  $\delta_2$  is fixed the thermodynamic state of the crystal depends only on the temperature. As shown in Fig.1, when we fix the value of  $\delta_2$ , the study of the thermal variation of the stable solution shows the presence of one or two first order phase transitions depending on whether  $\delta_2$  is smaller or larger than  $\delta_{2T}$ .

**Case  $\delta_2 = 14$**  At very low temperature,  $t = 0.001$ , the thermodynamic state is (0.000, 0.000). Increasing the temperature, the values of  $n_1$ ,  $n_2$ ,  $f$ ,  $s$  and  $u$  vary but there is only one stable state. At  $t = 2.917849$ , which corresponds

to point  $A_3$  in Fig.1, there are two stable states  $(1, 1)$  and  $(0.249, 0.043)$ . So, there is a first order transition between both states.

For the state  $(0.249, 0.043)$ , as for the state  $(0.000, 0.000)$ , the majority of the electronic subsystems (1) and (2) are in their fundamental level  $(a_1)$  and  $(a_2)$ , respectively. We say that those states belong to the thermodynamic phase  $(a, a)$ . For the state  $(1, 1)$  all the electronic subsystems (1) and (2) are in their excited level  $(b_1)$  and  $(b_2)$ , respectively. We say that this state belongs to the  $(b, b)$  phase. So, at  $t = 2.917849$ , we say that there is a first order phase transition between the  $(a, a)$  and  $(b, b)$  phases.

For  $t$  lower than the transition temperature, 2.917849, the stable state belongs to the  $(a, a)$  phase because  $n_1$  and  $n_2$  are lower than 0.5, and for  $t$  higher than 2.917849 the stable state belongs to the  $(b, b)$  phase because  $n_1$  and  $n_2$  are equal to 1..

We denote  $t_3$  the temperature of the transition  $(a, a) - (b, b)$ . So for  $\delta_2 = 14$ ,  $t_3 = 2.917849$ . In Fig.1, the curve with black circles represents the values of  $t_3$  for different values of  $\delta_2$  lower than  $\delta_{2T}$ . This curve is the  $(a, a) - (b, b)$  coexistence curve.

At the transition, the parameters  $n_i$  ( $i = 1, 2$ ),  $s$  and  $u$  display a discontinuity. We call  $(\Delta n_i)_3$  the discontinuity in  $n_i$ ,  $(\Delta s)_3$  that in  $s$  and  $(\Delta u)_3$  that in  $u$ . The value of the discontinuity in  $n_i$  is the value of  $n_i$  in the  $(1, 1)$  state minus its value in the  $(0.249, 0.043)$  state. So, for  $\delta_2 = 14$ , at  $t_3 = 2.917849$ ,  $(\Delta n_1)_3 = 0.751$  and  $(\Delta n_2)_3 = 0.957$ .

For  $\delta_2 = 14$ , at  $t_3 = 2.917849$ , the values of  $s$  and  $u$  for the  $(0.249, 0.043)$  state are 6.325423 and  $-3.050334$ , respectively, and they are 13.482498 and 17.832931, respectively, for the  $(1, 1)$  state. So, the discontinuity  $s$  is  $(\Delta s)_3 = 7.157075$  and that in  $u$  is  $(\Delta u)_3 = 20.883265$ .

We denote  $l_3$  the reduced latent heat for the  $(a, a) - (b, b)$  transition . We have

$$l_3 = t_3 (\Delta s)_3 \quad (82)$$

So, for  $\delta_2 = 14$ , at  $t_3 = 2.917849$ ,  $l_3 = 20.883264$ . We we can verify that  $l_3 = (\Delta u)_3$ .

**Case  $\delta_2 = 17$**  At very low temperature,  $t = 0.001$ , the thermodynamic state is  $(0.000, 0.000)$ . As the temperature increases, the values of  $n_1$ ,  $n_2$ ,  $f$ ,  $s$  and  $u$  but there is only one stable state. At  $t = 3.056919$ , which corresponds to point  $A_1$  in Fig.1, there are two stable solutions which are  $(1, 0.040)$  and  $(0.286, 0.020)$ .

The state  $(0.286, 0.020)$  belongs to the  $(a, a)$  phase. In the state  $(1, 0.040)$  all the electronic subsystems (1) are in their excited level  $(b_1)$  while the majority



of the electronic subsystems (2) are in their fundamental level ( $a_2$ ). We say that this state belongs to the  $(b, a)$  phase. So, at  $t = 3.056919$ , there is a first order phase transition between the  $(a, a)$  and  $(b, a)$  phases.

Above the temperature values 3.056919 and up to the temperature value 3.471697, which corresponds to point  $A_2$  in Fig.1, there is only one stable state  $(1, n_2)$ , where  $n_2$  varies from the value 0.040 to the value 0.079. It is clear that this state  $(1, n_2)$  belongs to the  $(b, a)$ . At the temperature value  $t = 3.471697$  there are two stable states which are  $(1, 1)$  and  $(1, 0.079)$ . So, at  $t = 3.471697$ , there is another first order phase transition between the  $(b, a)$  and  $(b, b)$  phases. In some case the value of  $n_2$  is higher than 0.5 for the state  $(1, n_2)$ . We consider that this state  $(1, n_2)$  belongs to the  $(b, a)$  phase even if the value of  $n_2$  is higher than 0.5.

In summary for temperature value lower than 3.056919 the stable state belongs to the  $(a, a)$  phase, between the temperature values 3.056919 and 3.471697 it belongs to the  $(b, a)$  phase and for temperature value higher than 3.471697 it belongs to the  $(b, b)$  phase because  $n_1$  and  $n_2$  are equal to 1..

We denote  $t_1$  the temperature of the transition  $(a, a) - (b, a)$  and  $t_2$  that of the transition  $(b, a) - (b, b)$ . So, for  $\delta_2 = 17$ ,  $t_1 = 3.056919$  and  $t_2 = 3.471697$ . In Fig.1, the curve with open circles and that with crosses represent the values  $t_1$  and  $t_2$ , respectively, for different values of  $\delta_2$  higher than  $\delta_{2T}$ . The first curve is the  $(a, a) - (b, a)$  coexistence curve and the second one the  $(b, a) - (b, b)$  coexistence curve.

At each of the two phase transitions, the parameters  $n_i$  ( $i = 1, 2$ ),  $s$  and  $u$  display a discontinuity. We call  $(\Delta n_i)_1$ ,  $(\Delta s)_1$  and  $(\Delta u)_1$  the values of this discontinuity at  $t_1$  and  $(\Delta n_i)_2$ ,  $(\Delta s)_2$  and  $(\Delta u)_2$  those values at  $t_2$ . It is worth to notice that  $(\Delta n_1)_2$  is always equal to zero.

We denote  $l_1$  the reduced the latent heat for the  $(a, a) - (b, a)$  transition and  $l_2$  that for the  $(b, a) - (b, b)$  transition. We have

$$l_1 = t_1 (\Delta s)_1 \tag{83}$$

and

$$l_2 = t_2 (\Delta s)_2 \tag{84}$$

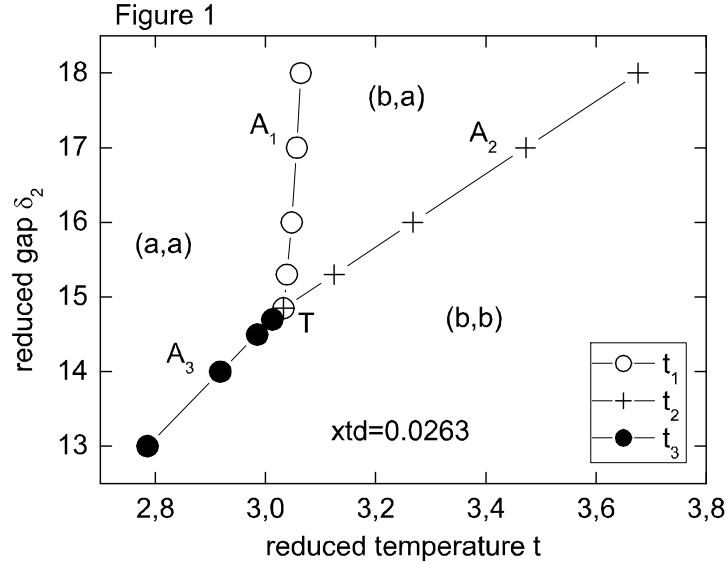


Fig. 1. Phase diagram for  $\tilde{x}$  constant. The symbol  $xtd$  stands for  $\tilde{x}$ . As the parameters  $\delta_1$ ,  $x$  and  $z$  are constant In this study a thermodynamic state depends on the three parameters  $t$ ,  $\delta_2$  and  $\tilde{x}$ . For given value to  $\delta_2$ , there are one or two first order phase transitions depending on the value of  $\delta_2$  compared to that of  $\delta_{2T}$ . We recall that in all this study  $\delta_1 = 10$ ,  $x = 10^{-5}$  and  $z = 0.2$ .

### 3.3.2 Triple point $T$

In Fig.1, the value of  $t_2$  minus that of  $t_1$ ,  $t_2 - t_1$ , is equal to 0.414778 for  $\delta_2 = 17$  and decreases when the value of  $\delta_2$  decreases. There is a value of  $\delta_2$  such as  $t_2$  is equal to  $t_1$ . Let us call  $\delta_{2T}$  this value. Similarly let us call  $t_T$  the value of  $t_1$  when  $t_1$  and  $t_2$  are equal. The set  $(\delta_{2T}, t_T)$  are the coordinates of the point  $T$  in Fig.1.

When  $t_1$  and  $t_2$  are equal, there are three stable solutions. In Fig. 1, those solutions are  $(0.280, 0.039)$ ,  $(1, 0.079)$  and  $(1, 1)$ . They belong to the  $(a, a)$ ,  $(b, a)$ , and  $(b, b)$  phases, respectively. The values of  $f$  for those solutions are  $-22.630346$ ,  $-22.630347$  and  $-22.630340$ , respectively. So we can say that the state  $T$  is a triple point. Indeed, in thermodynamics,  $\ll$  a state of three-phase comptability is a "triple point"  $\gg$ [9].

For each of the three stable solutions we can calculate the values of  $s$  and  $u$ . So, for the stable solutions  $(0.280, 0.039)$ ,  $(1, 0.079)$ , and  $(1, 1)$  the values of  $s$  are 6.489363, 9.048688, and 13.559420, respectively. Consequently, for the transition  $(a, a) - (b, a)$ ,  $(\Delta s)_1 = 2.559325$  and  $l_1 = 7.760728$ , for the transition  $(b, a) - (b, b)$ ,  $(\Delta s)_2 = 4.510740$  and  $l_2 = 13.678070$  and for the transition  $(a, a) - (b, b)$ ,  $(\Delta s)_3 = 7.070065$  and  $l_3 = 21.438799$ .

We introduce the following notations: the values of  $l_1$  and  $l_2$  at a triple point are denoted  $l_{1T}$  and  $l_{2T}$ , respectively. So, for  $\tilde{x} = 0.0263$  the triple point is characterized by the values  $\delta_{2T} = 14.84919$ ,  $t_T = 3.032334$ ,  $l_{1T} = 7.760728$  and  $l_{2T} = 13.678070$ . We recall that those values are obtained for  $\delta_1 = 10$ ,  $z = 0.2$  and  $x = 10^{-5}$ .

In fact, it is difficult to obtain the condition  $t_1 = t_2$ . We consider that this condition is reached when  $t_2 - t_1 \leq 5 \cdot 10^{-6}$ . We then take for  $t_T$  the value of  $t_1$  and for  $\delta_{2T}$  the corresponding value of  $\delta_2$ . When  $t_2 - t_1 \leq 5 \cdot 10^{-6}$  the difference between the three values of  $f$  is lower than  $10 \cdot 10^{-6}$ .

For each value of  $\tilde{x}$  there is a triple point characterized by the values  $\delta_{2T}$ ,  $t_T$ ,  $l_{1T}$  and  $l_{2T}$ . The variation of  $\delta_{2T}$  with the value of  $\tilde{x}$  is shown in Fig. 2, those of  $l_{1T}$  and  $l_{2T}$  in Fig. 3. As for  $t_T$ , it decreases from 3.081895 to 2.877612 when the value of  $\tilde{x}$  increases from  $5 \cdot 10^{-4}$  to  $10^{-1}$ .

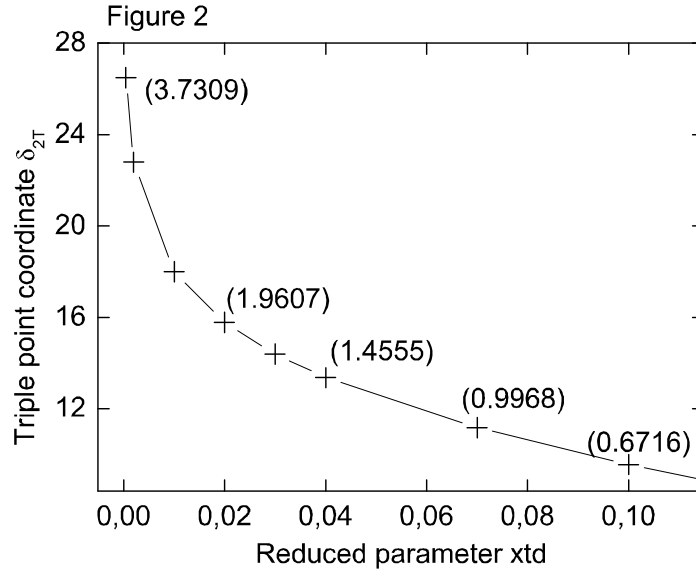


Fig. 2. Variation of  $\delta_{2T}$  with  $\tilde{x}$ . The parameter  $\delta_{2T}$  is the value of  $\delta_2$  at the Triple point. The numbers between brackets are the values of the ratio  $\frac{l_{2T}}{l_{1T}}$ . It is interesting to notice that for a value of  $\tilde{x}$  corresponds only one value of this ratio.

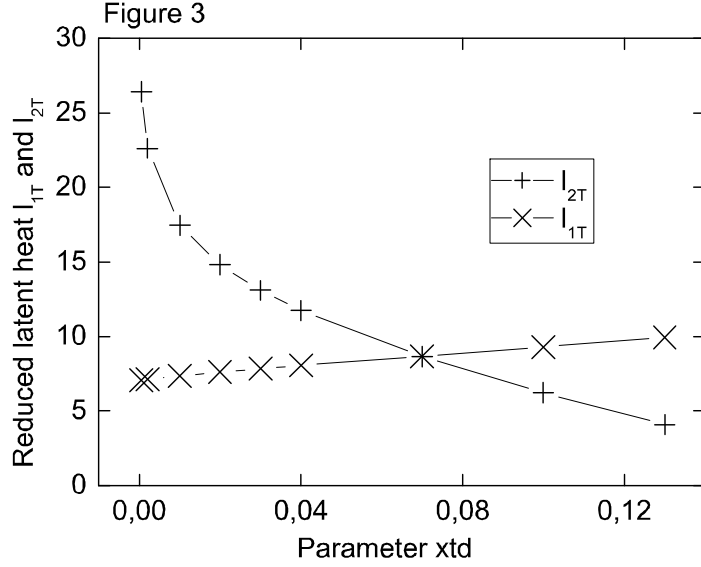


Fig. 3. Variation of  $l_{1T}$  and  $l_{2T}$  with  $\tilde{x}$ . The parameter  $l_{1T}$  is the value at the Triple point of the latent heat of the  $(a, a) - (b, a)$  phase transition and  $l_{2T}$  is that of the  $(b, a) - (b, b)$  phase transition. The value  $l_{2T}$  decreases when  $\tilde{x}$  increases and is equal to zero when  $\tilde{x}$  is higher than the critical value  $\tilde{x}_c$  which is near 0.166.

### 3.3.3 Critical value $\tilde{x}_C$

In the phase diagram of Fig.1,  $(\Delta n_2)_2$ , the value of the discontinuity in  $n_2$  along the  $(b, a) - (b, b)$  coexistence curve is constant and equal to 0.921. In a previous study [3], we have shown that  $(\Delta n_2)_2$  does not depend on the values of  $\delta_1$  and  $\delta_2$ , but depends only on that of  $\tilde{x}$ . The discontinuity value  $(\Delta n_2)_2$  decreases when  $\tilde{x}$  increases and is equal to zero when  $\tilde{x}$  is higher than a value called critical value of  $\tilde{x}$  and denoted  $\tilde{x}_C$ . For  $\tilde{x}$  higher than  $\tilde{x}_C$ , the first order  $(b, a) - (b, b)$

phase transition does not exist and the crystal passes from the  $(b, a)$  phase to the  $(b, b)$  phase continuously.

The value  $\tilde{x}_C$  is lower than 0.18. For  $\tilde{x}$  equal to 0.166 and 0.169,  $(\Delta n_2)_2$  is equal to 0.159 and 0.078, respectively. Taking into account the difficulty for working around the value  $\tilde{x}_C$ , we consider that the  $(b, a) - (b, b)$  phase transition does not exist when  $\tilde{x} > 0.166$  and we consider that the critical value  $\tilde{x}_C$  is equal to 0.166.

In this study, we have verify that the values of  $(\Delta s)_2$ ,  $(\Delta u)_2$ , and that of the latent heat  $l_2$  decrease when  $\tilde{x}$  increases and are nearly equal to zero when  $\tilde{x}$  is equal to 0.166.

The phase diagram of the crystal in the  $(\delta_2, t)$  plane for  $\tilde{x} = \tilde{x}_C = 0.166$  looks like that of Fig.1. So, for each value of  $\delta_2$ , larger than  $\delta_{2T}$ , there is a  $(b, a) - (b, b)$  phase transition and a transition temperature  $t_2$ . This value of  $t_2$  is the critical temperature value that we denote  $t_C$ . The variation of  $t_C$  with  $\delta_2$  is shown in Fig.4.

So, in this study, the critical point is characterised by  $\tilde{x} = \tilde{x}_C = 0.166$  and by the values of  $\delta_2$  and  $t$ .

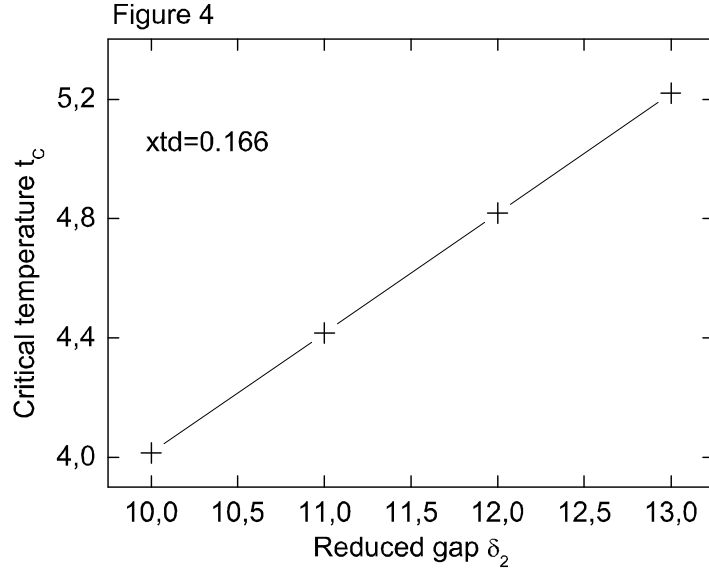


Fig. 4. Variation of the critical temperature  $t_C$  with  $\delta_2$ . The critical tem-

perature is the transition temperature  $t_2$  when the parameter  $\tilde{x}$  is equal to  $\tilde{x}_C = 0.166$ . The value  $\delta_2$  must be greater than the triple point value  $\delta_{2T}$  for  $x = \tilde{x}_C = 0.166$ .

### 3.4 Phase diagram for $\tilde{x}$ and $\delta_2$ varying

We look for a phase diagram where  $z$ ,  $\delta_1$  and  $x$  are constant while  $\delta_2$  and  $\tilde{x}$  can vary. We consider the case where the variations of  $\delta_2$  and  $\tilde{x}$  are controlled by a parameter  $P$  following the relations

$$\tilde{x} = \tilde{x}_0 + \tilde{c}P \quad (85)$$

and

$$\delta_2 = \delta_{20} + c_2P \quad (86)$$

where the coefficients  $\tilde{x}_0, \tilde{c}$ ,  $\delta_{20}$  and  $c_2$  are constants.

In order to give values to those coefficients, we use the experimental data concerning the phase diagram of carbon dioxide  $CO_2$ . So, we must assume that the phases  $(a, a)$ ,  $(b, a)$  and  $(b, b)$  of the model correspond to the solid, liquid and gas states, respectively and that  $P$  is the applied pressure. Consequently,  $l_1$  corresponds to the latent heat of fusion  $L_f$ ,  $l_2$  to the latent heat of vaporization  $L_v$  and  $l_3$  to the latent heat of sublimation  $L_s$ . We recall that  $z = 0.2$ ,  $\delta_1 = 10$  and  $x = 10^{-5}$ .

#### 3.4.1 Experimental data concerning $CO_2$

For  $CO_2$ , the coordinates of the triple point in the  $(P, T)$  diagram are  $P_T = 5.19bar$  and  $T_T = 216.55K$  and those of the critical point are  $P_C = 73.8bar$  and  $T_C = 304.25K$ . Moreover, for  $P = 1atm = 1.013bar$  the temperature of sublimation is  $T_s(1atm) = 194.67K$ . Concerning the latent heats : the values of the latent heat of fusion and of vaporization at the triple point are  $L_{fT} = 199kJkg^{-1}$  and  $L_{vT} = 350.83kJkg^{-1}$ , respectively. The latent heat of sublimation at  $1atm$  is  $L_s(1atm) = 573kJkg^{-1}$ . The latent heat  $L_{vT}$  has been obtained by extrapolating data found in gazechim website . All the other data are obtained from wikipedia website. We accept those experimental data and we shall show how they can be introduced in the model.

#### 3.4.2 Determination of the constants $\tilde{x}_0$ , $\tilde{c}$ , $\delta_{20}$ and $c_2$

**Triple point data** At the triple point of  $CO_2$  the ratio of the latent heats of vaporization and fusion,  $\frac{L_{vT}}{L_{fT}}$ , is equal to 1.7630.

We look for, in the model, the triple point for which the ratio  $\frac{l_{2T}}{l_{1T}}$  is equal to 1.7630. This triple point corresponds to  $\tilde{x} = 0.0263$  (see Fig. 2.). For this value of  $\tilde{x}$ , the latent heats  $l_1$  and  $l_2$  are equal to  $l_{1T} = 7.760728$  and  $l_{2T} = 13.678108$ , respectively, and then the ratio  $\frac{l_{2T}}{l_{1T}}$  is equal to 1.7625. Moreover for this value of  $\tilde{x}$ , the value of the parameter  $\delta_2$  is  $\delta_{2T} = 14.84919$  and the value of the triple point temperature is  $t_T = 3.032334$ .

As the pressure value at the triple point of  $CO_2$  is 5.19 bar, we can write the following equations

$$0.0263 = \tilde{x}_0 + \tilde{c} \cdot 5.19 \quad (1a)$$

$$14.84919 = \delta_{20} + c_2 \cdot 5.19 \quad (2a)$$

**Critical point data** For  $CO_2$ , the ratio of the values of the critical temperature and the triple point temperature,  $\frac{T_C}{T_T}$ , is equal to 1.4050.

We look for, in the model, the value  $t_C$  such as  $\frac{t_C}{t_T} = 1.4050$ . As we have obtained for  $t_T$  the value 3.032334, the reduced temperature  $t_C$  should be equal to 4.260429. As shown in Fig.4 the critical temperature value  $t_C$  depends on that of  $\delta_2$ . We look for the value of  $\delta_2$  such as  $t_C = 4.260429$ . This value is  $\delta_2 = 10.6115$ .

As the pressure value at the critical point of  $CO_2$  is 73.8 bar, we can write the following equations

$$0.166 = \tilde{x}_0 + 73.8 \tilde{c} \quad (1b)$$

$$10.6115 = \delta_{20} + 73.8 c_2 \quad (2b)$$

The solution of the system of equations (1a) and (1b) is

$$\tilde{x} = 15.732414 \cdot 10^{-3} + 2.036146 \cdot 10^{-3} P \quad (I)$$

The solution of the system of equations (2a) and (2b) is

$$\delta_2 = 15.16975 - 61.764903 \cdot 10^{-3} P \quad (II)$$

The relations (I) and (II) can be used above the triple point of  $CO_2$ , that is for  $P \geq 5.19$  bar.

**Data at  $P = 1atm$**  For  $CO_2$ , the ratio of the values of the sublimation temperature at the atmospheric pressure and the triple point temperature,  $\frac{T_s(1atm)}{T_T}$ , is equal to 0.8990. Moreover, the ratio of the values of the latent heat of sublimation at the atmospheric pressure and that of vaporization at the triple point,  $\frac{L_s(1atm)}{L_{vT}}$ , is equal to 1.6333.

We look for, in the model, a state on the  $(a, a) - (b, b)$  coexistence curve where  $t_3$  satisfies the relation  $\frac{t_3}{t_T} = 0.8990$  and where  $l_3$  satisfies the relation  $\frac{l_3}{l_{2T}} = 1.6333$ . As  $t_T$  is equal to 3.032334, the transition temperature  $t_3(1atm)$  should be equal to  $t_3(1atm) = 2.726068$ . As  $l_{2T}$  is equal to 13.678108, the reduced latent heat  $l_3(1atm)$  should be equal to  $l_3(1atm) = 22.340454$ . The state looking for is defined by a value for  $\tilde{x}$  and a value for  $\delta_2$ .

Let us use the relations (I) and (II). For  $P = 1atm = 1.013bar$ , those relations lead to the values  $\tilde{x}_{calc} = 0.017795$  and  $\delta_{2calc} = 15.107182$ . Using these values of  $\tilde{x}$  and  $\delta_2$  in the self-consistent equations we obtain for  $t_3$  and  $l_3$  the values  $t_{3calc} = 2.912993$  and  $l_{3calc} = 22.163028$ . We see that the set  $(l_{3calc}, t_{3calc})$  is different from the set  $(l_3(1atm), t_3(1atm))$ . This disagreement means that the relations (I) and (II) are not valid for  $P \leq P_T = 5.3 bar$ .

Finally, with  $\tilde{x} = 0.011625$  and  $\delta_2 = 14.720$ , the self-consistent equations lead to  $l_3 = 22.359920$  and  $t_3 = 2.724432$ . Those values are very near the set  $(l_3(1atm), t_3(1atm))$ .

We then can write for  $P = 1atm = 1.013 bar$  the following equations

$$0.011625 = \tilde{x}_0 + 1.013 \tilde{c} \quad (1c)$$

and

$$14.720 = \delta_{20} + 1.013 c_2 \quad (2c)$$

The solution of the system of equations (1a) and (1c) is

$$\tilde{x} = 8.06604 \cdot 10^{-3} + 3.51329 \cdot 10^{-3} P \quad (III)$$

The solution of the system of equations (2a) and (2c) is

$$\delta_2 = 14.688669 + 30.928896 \cdot 10^{-3} P \quad (IV)$$

The relations (III) and (IV) are valid for  $P \leq P_T$ .

In summary, for  $CO_2$  we have obtained the following values

$$t_T = 3.032334, t_C = 4.260429, t_3(1atm) = 2.726068 \quad (87)$$

$$l_{1T} = 7.760728, l_{2T} = 13.678108, l_3(1atm) = 22.340454 \quad (88)$$

and the relations (I) to (IV). Those results are obtained for  $\delta_1 = 10$ ,  $z = 0.2$  and  $x = 10^{-5}$ .



### 3.4.3 Use of the relations (I) to (IV)

The relations (I) to (IV) contain more informations than the set of reduced values obtained above in relations (87) and (88). Indeed, for each value of the applied pressure they allow to calculate the values of  $\tilde{x}$  and  $\delta_2$ . Then using the self-consistent equations we can calculate the values of the transition temperature  $t_1$ ,  $t_2$  and  $t_3$  and the values of the corresponding latent heat  $l_1$ ,  $l_2$  and  $l_3$ .

First, we have verified that using the relations (I) to (IV) we obtain for  $P = 5.19bar$  the values  $t_T$ ,  $l_{1T}$  and  $l_{2T}$  contained in relation (87) and (88), for  $P = 73.8bar$  the value  $t_C$  contained in relation (87) and for  $P = 1atm$  the values  $t_3(1atm)$  and  $l_3(1atm)$  contained in relation (87) and (88). Then, we have calculated the phase diagram of the crystal in the  $(P, t)$  plane and the variations with the applied pressure of the different latent heats.

The phase diagram in the  $(P, t)$  plane is shown in Fig.5. For  $P = 0bar$  the value of reduced temperature of sublimation is  $t_3(0bar) = 2.606381$ . As shown in Fig.5, the temperature of vaporization and that of sublimation increase when the applied pressure increases, which is in agreement with the experimental results. But the temperature of fusion decreases when the applied pressure increases. In this study, we have not analyse this last result which has been observed only for water,  $H_2O$ .

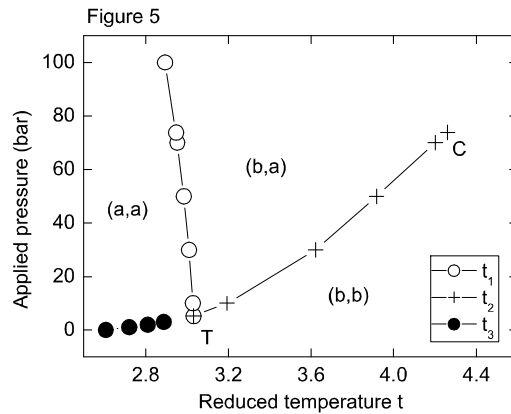


Fig. 5. Phase diagram obtained by using the relations (I) to (IV). It is assume that only the parameters  $\tilde{x}$  and  $\delta_2$  can vary with the applied pressure.

The variations with pressure of the different latent heats are shown in Fig.6. For  $P = 0\text{bar}$  the value of the latent heat of sublimation is  $l_3(0\text{bar}) = 22.685849$ .

For a given atom, when the electrons involved in the bonds are in their excited level, the increase of electronic energy is  $\delta_1 + \delta_2$ , in reduced unit. But the thermal energy necessary to move these electrons from their fundamental level to their excited one is  $l_3$ , the reduced latent heat of sublimation. As shown in Fig.6, this latent heat is lower than the sum  $\delta_1 + \delta_2$ . The values of the ratio  $l_3/(\delta_1 + \delta_2)$  is equal to 0.92 and to 0.91 for  $0\text{bar}$  and  $1\text{atm}$ , respectively. Likewise, for pressure values greater than  $P_T$  the reduced latent of fusion  $l_1$  is lower than the energy gap  $\delta_1$  which is equal to 10.

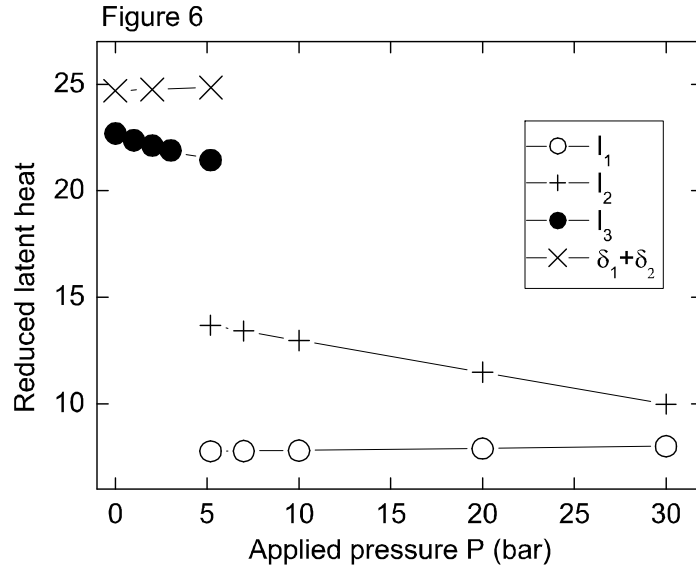


Fig. 6. Variation with pressure of the latent heat of fusion ( $l_1$ ), vaporization ( $l_2$ ) and sublimation ( $l_3$ ). The unit of energy is  $\hbar\omega_M(\lambda)$ .

For all substances the latent heat of vaporization decreases when the pressure increases and vanishes at the critical pressure. This result is verified in this study as seen in Fig.7.

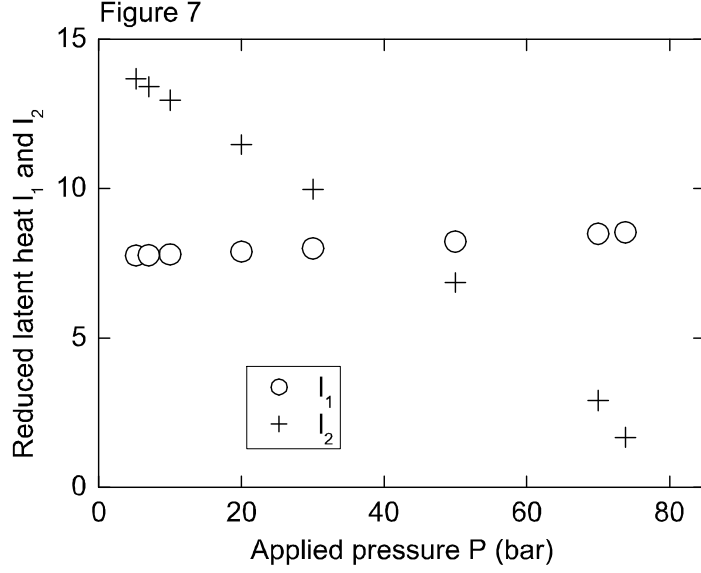


Fig.8. Variation with pressure of the latent heat of fusion ( $l_1$ ) and vaporization ( $l_2$ ). The pressure varies from  $P_T$  to  $P_C$ .

#### 3.4.4 Determination of the energy unit $\hbar\omega_M(\lambda)$

For the following, we use those numerical values : Boltzmann's constant  $k_B = 1.381 \cdot 10^{-23} J K^{-1}$ , elementary charge  $e = 1.602 \cdot 10^{-19} C$ , Avogadro's number  $N_A = 6.023 \cdot 10^{23} mol^{-1}$ , Planck's constant  $h = 6.626 \cdot 10^{-34} J s$  and  $\hbar = 1.055 \cdot 10^{-34} J s$ , Gas constant  $R = 8.314 J mol^{-1} K^{-1}$ , molar mass of  $CO_2$   $M = 44 g$ .

If we assume that  $t_T$  is the reduced value of the experimental transition temperature  $T_T$  we can write

$$\frac{k_B T_T}{\hbar\omega_M(\lambda)} = t_T \quad (89)$$

So

$$\hbar\omega_M(\lambda) = \frac{k_B T_T}{t_T} \quad (90)$$

With  $T_T = 216.55 K$  and  $t_T = 3.032334$  the energy unit is equal to

$$\hbar\omega_M(\lambda) = 98.622 \cdot 10^{-23} J = 61.562 \cdot 10^{-4} eV \quad (91)$$

Using this value for  $\hbar\omega_M(\lambda)$  we obtain for the critical temperature

$$\frac{\hbar\omega_M(\lambda)t_C}{k_B} = 304.25K \quad (92)$$

and for temperature of sublimation at the atmospheric pressure

$$\frac{\hbar\omega_M(\lambda)t_3(1atm)}{k_B} = 194.68K \quad (93)$$

Both calculated values are equal to the experimental values. So, if we pass from the phase diagram in the  $(P, t)$  plane to the phase diagram in the  $(bar, Kelvin)$  plane by using this value for the energy unit, the values of the triple point temperature, the critical temperature and the sublimation temperature at the atmospheric pressure are equal to the respective experimental values. The transition temperature values for other values of the pressure depend on the relation (I) to (IV).

Using  $l_{2T} = 13.678070$  and this energy unit we can calculate the latent heat of vaporization at the triple point. So

$$\frac{1000}{44}N_A l_{2T} \hbar\omega_M(\lambda) = 185kJ kg^{-1} \quad (94)$$

In relation (94)  $\frac{1000}{44}$  is the number of mole per  $kg$ . This value,  $185kJ kg^{-1}$ , is different from the experimental value  $L_{vT} = 350.83kJ kg^{-1}$ . For the latent heat of fusion at the triple point and that of sublimation at the atmospheric pressure the calculated values are  $104.8kJ kg^{-1}$  and  $301.6kJ kg^{-1}$ . Both calculated values are different from the experimental values which are equal to  $199kJ kg^{-1}$  and  $573kJ kg^{-1}$ , respectively. These disagreements between the calculated values for the latent heats and the experimental one are discussed in the next section. We think that a part of the disagreement comes from the fact that the sum  $\sum_{(\bar{k})}'$  is made on two phonon branches and not three.

The parameter  $\Delta_1$ , which is constant, is equal to

$$\Delta_1 = \hbar\omega_M(\lambda) \delta_1 = 61.562 \cdot 10^{-3} eV$$

The parameter  $\delta_2$  varies with the pressure. Its value for  $P = 0$  is 14.688669. So, for  $P = 0$  the value of  $\Delta_2$  is  $\Delta_2(0bar)$  with

$$\Delta_2(0bar) = 90.426 \cdot 10^{-3} eV$$

## 4 Conclusion and discussion

To apply the model to the study of the phase diagram of a substance, we have assumed that the phases  $(a, a)$ ,  $(b, a)$  and  $(b, b)$  of the model correspond to the solid, liquid and gas states, respectively. And consequently,  $l_1$  corresponds to the latent heat of fusion  $L_f$ ,  $l_2$  to the latent heat of vaporization  $L_v$  and  $l_3$  to the latent heat of sublimation  $L_s$ . Moreover, we have assumed that the parameters  $z$ ,  $\delta_1$  and  $x$  are constant while the parameters  $\delta_2$  and  $\tilde{x}$  vary linearly with the applied pressure  $P$ . The parameters  $\delta_1$  and  $x$  refer to the chemical bond between two atoms nearest-neighbors and the parameters  $\delta_2$  and  $\tilde{x}$  refer to the chemical bond between two atoms next nearest-neighbors. Taking into account the experimental data of  $CO_2$  we get the reduced values contained in the relations (87) and (88) and the equations (I) to (IV). By using the self-consistent equations, these equations allow to determine the phase diagram of  $CO_2$  in the plane  $(P, t)$  and the reduced values of the latent heat in the different first-order transitions (fusion, vaporization and sublimation),  $t$  being the reduced temperature, We obtain the results in *Kelvin* and *Joule* by multiplying the reduced values by the energy unit  $\hbar\omega_M(\lambda)$ . From equation (89) the energy unit is chosen so that the calculated value in *Kelvin* of the triple point temperature is equal to the experimental value.

### 4.1 Meaning of the results

The parameter  $x$  is the ratio  $\frac{\nu}{\lambda}$ , where  $\lambda$  is the value in the solid state of elastic constant of the elastic spring which links two atoms nearest-neighbors and  $\nu$  is its value in the liquid and gas states. The value  $x = 10^{-5}$  means that the value of  $\nu$  is zero. So, in the liquid and gas phases the spring does not exist neither does the chemical bond. Moreover this result means that the value of the parameter  $\Delta_1$  is that of the energy of the chemical bond between two nearest-neighbors atoms.

As for the elastic constant of the spring which links two atoms next nearest-neighbors its value is never zero. Consequently, the chemical bond between two atoms next nearest-neighbors exists in the three phases. Concerning the gas phase, this result is contained in the van der Waals equation.

As shown in Fig.6 the latent heat of sublimation  $l_3$  is smaller than the electronic energy  $\delta_1 + \delta_2$ . This result is contained in the expression of the internal energy  $U$  and is independent of relations (I) to (IV) as explained below.

In the  $(a, a)$  phase,  $m_1$  and  $m_2$  are equal to  $-1$  and they are equal to  $1$  in the  $(b, b)$  phase. Calling  $U_{(a,a)}$  and  $U_{(b,b)}$  the values of the internal energy in the  $(a, a)$  and  $(b, b)$  phases, respectively, we have from relation (70)

$$U_{(b,b)} - U_{(a,a)} = N(\Delta_1 + \Delta_2) - (U_{vib(a,a)} - U_{vib(b,b)}) \quad (95)$$

As the values of the elastic force constants are lower in the  $(b, b)$  phase than in the  $(a, a)$  phase, the value of the vibration energy in the  $(b, b)$  phase,  $U_{vib(b,b)}$ , is lower than its value in the  $(a, a)$  phase,  $U_{vib(a,a)}$ . So the variation of internal energy is less than the variation of electronic energy,  $N(\Delta_1 + \Delta_2)$ .

## 4.2 Comments on the results

The method used to introduce the experimental data of the substance into the model causes that if the *Kelvin* value of one of the three reduced temperatures  $t_T$ ,  $t_C$  and  $t_3(1atm)$  (relations 87) is equal to the corresponding experimental value it is the same for the other two values. The use of relation (89) imposes that the *Kelvin* value of  $t_T$  is equal to the experimental value of the triple point temperature of  $CO_2$ . So three points of the phase diagram of the compound in the plane (*bar, Kelvin*) agree with the experimental data whatever the values of the coefficients of equations (I) to (IV), that is whatever the values of  $\delta_1$  and  $z$ .

Likewise, if the *Joule* value of one of the three reduced latent heats  $l_{1T}$ ,  $l_{2T}$  and  $l_3(1atm)$  (relations 88) is equal to the corresponding experimental value it is the same for the other two values. With the energy unit given by relation (89), the *Joule* value of  $l_{2T}$  is equal to  $185kJ kg^{-1}$  while the experimental value of the latent heat of vaporization at the triple point is equal to  $350,83kJ kg^{-1}$ . We think that the disagreement between these two values comes from the fact the values of  $\delta_1$  and  $z$  used in this study are arbitrary values. It would be interesting to see how vary all the results obtained when one varies the values of  $\delta_1$  and  $z = \frac{\tilde{\lambda}}{\lambda}$ .

The study of speed of sound in the crystal at low temperature should make it possible to determine the values of the elastic constants  $\lambda$  and  $\tilde{\lambda}$ . We then can deduce the value of the report  $z = \frac{\tilde{\lambda}}{\lambda}$  and that of the energy unit  $\hbar\omega_M(\lambda)$ . Let us denote by  $(\hbar\omega_M(\lambda))_{sound}$  this value. Using relation (89) we write

$$\frac{k_B T_T}{t_T} = (\hbar\omega_M(\lambda))_{sound} \quad (96)$$

As the value of  $t_T$  depends on those of  $\delta_1$  and  $z$ , we seek the value of  $\delta_1$  so that this relation is satisfied.

For some substances, the ratio  $L_{vT}/L_{fT}$  is equal to 10. In Fig.3, the highest value for the ratio  $\frac{l_{2T}}{l_{1T}}$  is around 4. Preliminary calculations show that the value of the ratio  $\frac{l_{2T}}{l_{1T}}$  increases when  $z$  increases, the value of  $\delta_1$  being fixed.

Moreover, we think that the slope of the  $(a, a) - (b, a)$  coexistence curve in Fig. 5 depends on the values of the coefficients of relation (I) to (IV) and then it depends on the values of  $\delta_1$  and  $z$ .

### 4.3 Conclusion

Having found the values of  $\delta_1$  and  $z$  for the substance, we can carry out the study describe here. This study is based on the fact that when atoms ( or molecules) have two energy levels an atom-vibrations coupling can exist. Spin conversion compounds are an example of such coupling.

The author has done alone this study and has written alone this manuscript.

## APPENDIX

### 4.4 Phonon dispersion relations for the square lattice

The dispersion relations for the two acoustics branches are

$$\omega_1 = \left( \frac{1}{2} \left( c_1 + c_2 + \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right) \right)^{1/2}$$

$$\omega_2 = \left( \frac{1}{2} \left( c_1 + c_2 - \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right) \right)^{1/2}$$

with

$$c_1 = \frac{2E}{m_a} (1 - \cos k_x a) + \frac{2\tilde{E}}{m_a} (1 - \cos k_x a \cos k_y a)$$

$$c_2 = \frac{2E}{m_a} (1 - \cos k_y a) + \frac{2\tilde{E}}{m_a} (1 - \cos k_x a \cos k_y a)$$

$$c_3 = \frac{2\tilde{E}}{m_a} \sin k_x a \sin k_y a$$

In the above relations,  $m_a$  is the atoms mass,  $a$  is the distance of the equilibrium positions of the atoms,  $E$  and  $\tilde{E}$  are the elastic force constants for atoms pairs first neighbors and second neighbors, respectively.

With the boundary periodic conditions, the components  $k_x$  and  $k_y$  of the wave vectors  $\vec{k}$  are

$$k_x = \alpha_x \frac{2\pi}{N_1 a} \quad \text{and} \quad k_y = \alpha_y \frac{2\pi}{N_2 a}$$

with  $\alpha_x = 0, \pm 1, \pm 2, \dots, \pm \left(\frac{N_1}{2} - 1\right), \frac{N_1}{2}$  and  $\alpha_y = 0, \pm 1, \pm 2, \dots, \pm \left(\frac{N_2}{2} - 1\right), \frac{N_2}{2}$ .

The wave vector  $\vec{k} (0, 0)$  corresponds to a translation mode. So, there are  $N_1 N_2 - 1$  different wave vectors which correspond to phonon frequency values.

The parameters  $N_1, N_2$  and  $a$  are defined in the text.

#### 4.5 Calculation of the partial derivatives $\frac{\partial \omega}{\partial E}$ and $\frac{\partial \omega}{\partial \tilde{E}}$

We introduce  $r$  by

$$\omega = \sqrt{r}$$

with

$$r = \frac{1}{2} \left( (c_1 + c_2) \pm \sqrt{(c_1 - c_2)^2 + 4c_3^2} \right)$$

We can write

$$r = \frac{1}{2} \left( \frac{2E}{m_a} d_1 + \frac{4\tilde{E}}{m_a} d_2 \pm \sqrt{\left(\frac{2E}{m_a}\right)^2 d_3^2 + 4 \left(\frac{2\tilde{E}}{m_a}\right)^2 d_4^2} \right)$$

or

$$r = \frac{E}{m_a} d_1 + \frac{2\tilde{E}}{m_a} d_2 \pm \sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}$$

where

$$d_1 = 2 - \cos k_x a - \cos k_y a$$

$$d_2 = 1 - \cos k_x a \cos k_y a$$

$$d_3 = \cos k_y a - \cos k_x a$$

$$d_4 = \sin k_x a \sin k_y a$$

So we have

$$\frac{\partial \omega}{\partial E} = \frac{1}{2\omega} \frac{\partial r}{\partial E}$$

with

$$\frac{\partial r}{\partial E} = \frac{1}{m_a} \left( d_1 \pm \frac{E}{m_a} \frac{d_3^2}{\sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}} \right)$$

and

$$\frac{\partial \omega}{\partial \tilde{E}} = \frac{1}{2\omega} \frac{\partial r}{\partial \tilde{E}}$$



with

$$\frac{\partial r}{\partial \tilde{E}} = \frac{1}{m_a} \left( 2d_2 \pm \frac{4\tilde{E}}{m_a} \frac{d_4^2}{\sqrt{\frac{E^2}{m_a^2} d_3^2 + \frac{4\tilde{E}^2}{m_a^2} d_4^2}} \right)$$

For some values of wave vector components  $(k_x, k_y)$  the parameter  $d_4$  is equal to zero. In that case the above relations are modified. So,  $r$  becomes

$$r = \frac{E}{m_a} d_1 + \frac{2\tilde{E}}{m_a} d_2 \pm \frac{E}{m_a} |d_3|$$

the parameters  $\frac{\partial r}{\partial E}$  and  $\frac{\partial r}{\partial \tilde{E}}$  become

$$\frac{\partial r}{\partial E} = \frac{d_1}{m_a} \pm \frac{|d_3|}{m_a}$$

and

$$\frac{\partial r}{\partial \tilde{E}} = \frac{2d_2}{m_a}$$

where  $|d_3|$  is the absolute value of  $d_3$

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