SIMULACIO MONTE CARLO DE SISTEMES AMB ACOBLAMENT DE GRAUS DE LLIBERTAT.
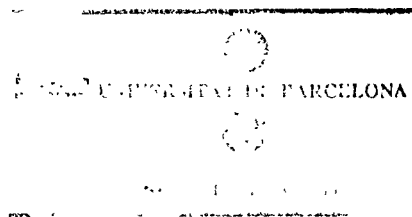
4.- APPLICATION TO A DISPLACIVE PHASE TRANSITION IN A BINARY ALLOY

Let us consider a binary alloy that undergoes, at T_0, a structural first-order phase transition (SPT) and an order-disorder transition (ODT) at $T_c > T_0$. This system is exemplified by a bcc A_xB_{1-x} binary alloy which shows at low (or relatively low) temperatures a martensitic transition (MT) and well above an ODT. Specific examples are the ß-CuZn and the ß-CuAl alloys [9].

Let x_i (i = 1,..,N) be the positional coordinates of the particles in the lattice. The structural first-order phase transition will be, conversely to the Potts model described in section 3, associated to continuous degrees of freedom. We also need a set of variables $\sigma = \{\sigma_1, \sigma_2, \ldots \sigma_N\}$ in order to describe the atom distribution over the different lattice sites. σ_i takes the value 1 (-1) when the lattice site i is occupied by an atom A (B).

We assume that the value of σ can be changed by quenching from T_i to a low enough temperature T_f as explained before. The state obtained in this way will be a long-lived metastable state which does not change , at least at the usual experimental time-scales.

4.1.- Calculation of $\delta\Delta E$
The Hamiltonian for this system can be written as:

$$H = \sum_{\langle ij \rangle} [\epsilon_{AA}(x_{ij})\delta(\sigma_i - 1)\delta(\sigma_j - 1) + \epsilon_{AB}(x_{ij})(\delta(\sigma_i + 1)\delta(\sigma_j - 1) +$$
$$+ \delta(\sigma_i - 1)\delta(\sigma_j + 1)) + \epsilon_{BB}(x_{ij})\delta(\sigma_i + 1)\delta(\sigma_j + 1)]$$

(20)

where the summation extends over all the ij pairs (separated by distances x_{ij}). $\epsilon_{\alpha\beta}(x)$ (α,β = A,B) are the pair-interaction potentials assumed to be central.

Most of the bcc alloys undergoing a MT have a DO_3 or a $L2_1$ ordered structure [9]. In order to compare our results with experimental data we consider a bcc binary alloy which undergoes two order-disorder transitions. A DO_3(or $L2_1$) → B2 transition at T_{c2} and a B2 → A2 (disordered alloy) transition at $T_{c1} \gg T_{c2}$ ($\gg T_0$). For the sake of simplicity we assume that the structure of the L-phase is fcc which can be obtained from the bcc H-phase through a Bain distortion mechanism [14] (Fig. 4).

We divide the bcc lattice into four sublattices (see Fig. 1). If the fraction of A atoms x > 0.50 then the $L2_1$ is defined by $P_A^1 = P_A^2 \neq P_A^3 \neq P_A^4$, where P_α (α= A,B and i=1,2,3,4) are the occupation probabilities (directly related to the σ_i variables). The DO_3 ordered structure is defined by $P_A^1 = P_A^2 = P_A^3 \neq P_A^4$. Due to the diffusionless character of the MT, the distribution of atoms (occupation probabilities) will be the same in the H-phase and in the L-phase.

Note that in the (bcc) H-phase a given atom has z_1 = 8 n.n. and z_2 = 6 next nearest neighbours (n.n.n.). The z_1 n.n. are also n.n. in the fcc phase, four of the z_2 n.n.n. in the bcc phase transform in n.n. in the fcc phase and the other two n.n.n. become n.n.n. in the L-phase.

We extend the summation in (20) to the minimum range to assure mechanical stability for both structures.

In the H-phase we consider pair-wise interactions up to n.n.n.

The energy of the system in the H-phase E_H is :

$$E_H = [\sum_{\alpha\beta} N_{\alpha\beta}^{(1)}\ \epsilon_{\alpha\beta}^{(1)} + \sum_{\alpha\beta} N_{\alpha\beta}^{(2)}\ \epsilon_{\alpha\beta}^{(2)}] \tag{21}$$

while in the fcc phase we consider only interactions up to n.n:

$$E_L = \sum_{\alpha\beta} \hat{N}_{\alpha\beta}^{(1)}\ \hat{\epsilon}_{\alpha\beta}^{(1)} \tag{22}$$

where $N_{\alpha\beta}^{(i)}$ ($\hat{N}_{\alpha\beta}^{(i)}$) is the number of ith-neighbour $\alpha\beta$ pairs in the H (L) phase. $\epsilon_{\alpha\beta}^{(i)}$ ($\hat{\epsilon}_{\alpha\beta}^{(i)}$) is the interaction energy corresponding to the value of $\epsilon_{\alpha\beta}(x)$ at the equilibrium distance between the ith-neighbour pairs in the H (L) phase. In principle we should consider that the $\epsilon_{\alpha\beta}$ energies depend on σ. Nevertheless we will consider that the Bain distortion associated to the transformation from the H to the L phase does not depend on the frozen internal state of the system. We will return to this point later.

Given that σ remains unchanged by the MT, the energy shift $\delta\Delta E$ associated to a change from σ to $\sigma'$is:

$$\delta\Delta E = [E_L(\sigma') - E_H(\sigma')] - [E_L(\sigma) - E_H(\sigma)]$$

$$= [E_L(\sigma') - E_L(\sigma)] - [E_H(\sigma') - E_H(\sigma)] = \delta E_L - \delta E_H \tag{23}$$

Taking into consideration that:

$$\hat{N}_{\alpha\beta}^{(1)} = N_{\alpha\beta}^{(1)} + \tfrac{2}{3}\ N_{\alpha\beta}^{(2)} \tag{24}$$

a straightforward calculation gives:

$$\delta\Delta E = (\hat{V}^{(1)} - V^{(1)})\ \delta N_{AB}^{(1)} + (\ \tfrac{2}{3}\ \hat{V}^{(1)} - V^{(2)})\ \delta N_{AB}^{(2)} \tag{25}$$

where $V^{(i)} = \epsilon_{AB}^{(i)} - \tfrac{1}{2}(\epsilon_{AA}^{(i)} + \epsilon_{BB}^{(i)})$ and $\hat{V}^{(i)} = \hat{\epsilon}_{AB}^{(i)} - \tfrac{1}{2}(\hat{\epsilon}_{AA}^{(i)} + \hat{\epsilon}_{BB}^{(i)})$ are the ordering energies in the H and L-phase respectively.

When $T_{c1} > T_{c2}$, for quenches from temperatures higher (or slightly higher) than T_{c2}, the number of n.n. AB pairs remain nearly constant [15]. One can then write:

$$\delta\Delta E \cong (\ \tfrac{2}{3}\ \hat{V}^{(1)} - V^{(2)})\ \delta N_{AB}^{(2)} \tag{26}$$

4.2.- Calculation of $\delta\Delta S$

Let us assume that the entropy change for the transition from the H-phase to the L-phase is given by [16]:

$$\Delta S = 3Nk_B \ln (w_H/w_L) \tag{27}$$

where w_H and w_L are low temperature Einstein frequencies corresponding to the H and L phases respectively. Equation (27) is appropriate for temperatures $T > T_E = hw/k_B$.

The change in the Einstein frequency from the H to the L-phase is due to both changes in the geometry and changes in the strength of bonds (interaction energies) between atoms. C_1 and C_2 represent, respectively, the strength of n.n. and n.n.n. bonds between atoms. For $C_1 \gg C_2$ then [16]:

$$w_H = (z_1 C_1 + z_2 C_2)^{1/2} \tag{28}$$

In the hypothesis of central forces the elastic constants C_{44} and $C' = 1/2(C_{11} - C_{12})$, depend only on C_1 and C_2 respectively in such a way that:

$$(C_{11} - C_{12})/C_{44} = 2\ C_2/C_1 = (2A)^{-1} \tag{29}$$

where A is the elastic anisotropy. For the alloys transforming martensitically A is large (it varies from 10 to 15 in Cu-based alloys) which justifies the assumption that $C_1 \gg C_2$. We now assume that the change in C_1 can be neglected. Considering, as before, only n.n. interactions in the L-phase, we obtain:

$$\Delta S = 3/2\ Nk_B \ln\{(z_1 + z_2/2A)/\hat{z}_1\} \tag{30}$$

where $\hat{z}_1 = 12$ is the number of n.n. in the fcc phase. Now:

$$\delta\Delta S = \Delta S(\sigma') - \Delta S(\sigma) =$$
$$= 3/2\ Nk_B \ln\{(1 + \alpha A^{-1}(\sigma'))/(1 + \alpha A^{-1}(\sigma))\} \tag{31}$$

where $\alpha = z_2/z_1$. Taking into account that αA^{-1} is small, equation

(31) can be rewritten as:

$$\delta \Delta S = \frac{3}{2} N k_B \alpha \left[\frac{1}{A(\sigma')} - \frac{1}{A(\sigma)} \right] \approx \frac{3}{2} N k_B \alpha \left[1 - \frac{\delta C_{44}}{\delta C'} \frac{C'}{C_{44}} \right] \frac{\delta C'}{C_{44}} \qquad (32)$$

where $\delta C' = C'(\sigma') - C'(\sigma)$ and $\delta C_{44} = C_{44}(\sigma') - C_{44}(\sigma)$.

In the central-potential approximation, C_{44} depends only on n.n. AB pairs [15]. Since this kind of pairs is not affected by the quench then:

$$\delta \Delta S \cong 3/2 \ N k_B \alpha (\delta C'/C_{44}) \qquad (33)$$

where $\delta C'$ can be written in terms of $\delta N_{AB}^{(2)}$ [15], resulting that $\delta \Delta S$ is proportional to $\delta N_{AB}^{(2)}$.

It is interesting to notice that for the kind of alloys considered here, $\delta C'/C_{44} \ll 1$. For example, for the Cu-Zn-Al alloy (studied in section 4.3), this ratio can be evaluated using elastic constant values taken from reference [17]. One then obtains that $\delta \Delta S/\Delta S < 0.01$. Hence, from equations (4) and (26) we obtain:

$$\delta T_0 = \delta \Delta E/\Delta S = (1/\Delta S)/(\ 2/3 \ \hat{V}^{(1)} - V^{(2)}) \ \delta N_{AB}^{(2)} \qquad (34)$$

where now ΔS can be taken as constant.

Using standard mean-field theory one can calculate $\delta N_{AB}^{(2)}$. We define, in terms of the occupation probabilities, the following long-range order parameter (LROP) Σ:

$$\Sigma = (p_A^L - p_B^2) - (4x-3) \qquad (35)$$

The ordered structure is supposed to be of the $L2_1$ type for $0.5 < x < 0.75$, and of the DO_3 type for $x = 0.75$ [15]. It is easy to see that:

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$$\delta N_{AB}^{(2)} = \tfrac{1}{4} N(\Sigma^2 - (4x-2)^2) \tag{36}$$

Introducing (36) in (34) one gets:

$$\delta T_0 \cong (1/\Delta S)(2/3\hat{V}^{(1)} - V^{(2)})(\Sigma^2 - (4x-2)^2) \tag{37}$$

The dependence of δT_0 on Σ^2 has already been predicted in the frame of the Landau theory [11]. Here we obtain (37) from a more microscopic justification.

4.3.- Comparison with experimental results

Given that, to our knowledge, no experimental results are available for binary alloys, we compare our theoretical predictions with data corresponding to the Cu-(Zn-Al) ternary system. Nevertheless it can be regarded as a binary-like system. This is because the ordering energy for Cu-Al pairs is only around 1.5 times greater than the ordering energy for Cu-Zn pairs but 20 times greater than the corresponding to Zn-Al pairs [9]. We then assume:

$$\hat{V}^{(1)} = (x_{Zn}V^{(1)} + x_{Al}V^{(1)})/(1-x) \tag{38a}$$

$$V^{(2)} = (x_{Zn}V^{(2)} + x_{Al}V^{(2)})/(1-x) \tag{38b}$$

where x_{Zn} and x_{Al} are the atomic fractions of Zn and Al respectively, and $V^{(k)}{}_{\alpha-\beta}$ ($\hat{V}^{(k)}{}_{\alpha-\beta}$) are the ordering energies between k-th $\alpha-\beta$ pairs in the H (L) phase.

Within the composition of interest x 0.65 the $Cu_x(Zn-Al)_{1-x}$ shows, at low temperatures, a $L2_1$ structure and a B2 structure at higher temperatures. In this case, the ordering energies in the H and L-phases have been evaluated for the different atom pairs [9]. For the particular alloy: Cu; 28.09at%Zn; 9.95at%Al, we obtain (in units of R) $\hat{V}^{(1)} = 863$ K and $V^{(2)} = 610$ K. Taking $\Delta S = -1.30$ J/Kmol [18], equation (37) leads to a maximum shift of the transition

temperature of $\delta T_{0max} = -38$ K while the maximum value obtained experimentally is $(\delta T_0)_{exp} = -62$ K [19]. For the Cu_3Al alloy, $\hat{V}^{(1)} = 1250$ K and $V^{(2)} = 825$ K, and the maximum shift predicted is $\delta T_{0max} = 49$ K of opposed sign to the previous case. This result is consistent with experiments carried out on Cu-(Al-Be) with x = 0.74 and only a 2 at% of Be for which a positive shift of T_0 after quench has been recently obtained [20].

In fig.5 we present for the Cu; 16 at%Zn; 16 at% Al alloy, the measured δT_0 as a function of the relative change $\Delta I/I$ in X-ray intensity of 111 superlattice reflections [21]. The 111 superlattice reflections arise from the L_{21} ordering. Measurements correspond to different T_q-temperatures. In spite of experimental uncertainties, results show a quite good correlation between ordering and transition temperature shift. However more accuracy is needed to justify the explicit dependence predicted in equation (36). Furthermore, in agreement with our assumption of neglecting contributions coming from $\delta N_{AB}^{(A)}$, the intensity of the 200 superlattice reflections arising from the B2 ordering, present a very small dependence on T_q [21].

DISCUSSION

In this paper we address our attention to two different examples of systems undergoing a diffusionless first-order phase transition which thermodynamic properties depend on the internal state at which the transition takes place. Associated to the degrees of freedom describing this internal state, the system exhibits a secondary phase-transition at a higher temperature, distant from the diffusionless first-order, or primary phase transition. The internal state can then be changed by means of a fast quench and one can study the coupling effects between the ordering modes associated to both phase transitions.

In the first example, we consider a three-state Potts model in a system with two kind of particles arranged on a regular lattice. The specification of the particle distribution on the different lattice sites, determines the internal state of the system. We find that changes on such internal state produce a shift in the primary transition temperature, which is associated to shifts in both energy and entropy changes. The shift in the entropy change between both, high and low temperature phases, is related to different values of the discontinuity of the Potts order-parameter at the first-order transition point. The shift in the energy change is associated with the different distribution of particles which provokes variations in the effective interactions.

In the second example, we analyze a metallic binary alloy which undergoes a displacive transition of the martensitic type from a b.c.c. structure to a more compact phase (for instance a f.c.c). These systems are characterized by a large elastic

anisotropy. This property is intimately related to the directional character of the MT mechanism which is mainly described by a shear deformation associated to the C' elastic constant. This favours that the entropy change between both phases depends only very weakly on the ordering state of the system. When only the DO_3 ordering (associated to n.n.n. pairs) is changed, the shift in the entropy change is proportional to the ratio $\delta C'/\delta C_{44}$ (33), which in turn is vanishingly small. In a more general situation, when changes in both n.n. and n.n.n. pairs are induced, from equation (32), we expect that the assertion concerning to the weak dependence of the entropy change on the ordering state be right as well. Consequently, the final low-temperature structure is, in this case, independent of the internal state of the system and the corresponding interaction pair energies are now independent on the ordering state. The transition temperature shift is then only associated to a shift in the energy change which, in turn, will depend only on changes of the n.n.n. AB pairs (34).

In terms of a Landau description, a φ-6 free-energy expansion in the primary order parameter (related to the deformation) has been proposed to describe MT [23]. The simplest suitable coupling-term is then biquadratic in both order parameters. This coupling gives rise to formally the same results explained above. This Landau model has been previously discussed in the context of the MT [11]. Here we proceed further and show that the displacive character of the structural transition is not a definitive condition to assure that the shift of the entropy change is zero for different ordering states. Also the large elastic anisotropy

together with symmetry characteristics of the transition mechanism are relevant for this condition to be satisfied.

In the case of the three-state Potts model, the description of the first-order transition needs a cubic term in the Landau free-energy expansion [13]. The coupling with the frozen internal degrees of freedom can be introduced, at least, by means of a cubic-quadratic term in the primary and secondary order parameters respectively. This minimal model is qualitatively consistent with the mean-field results discussed above.

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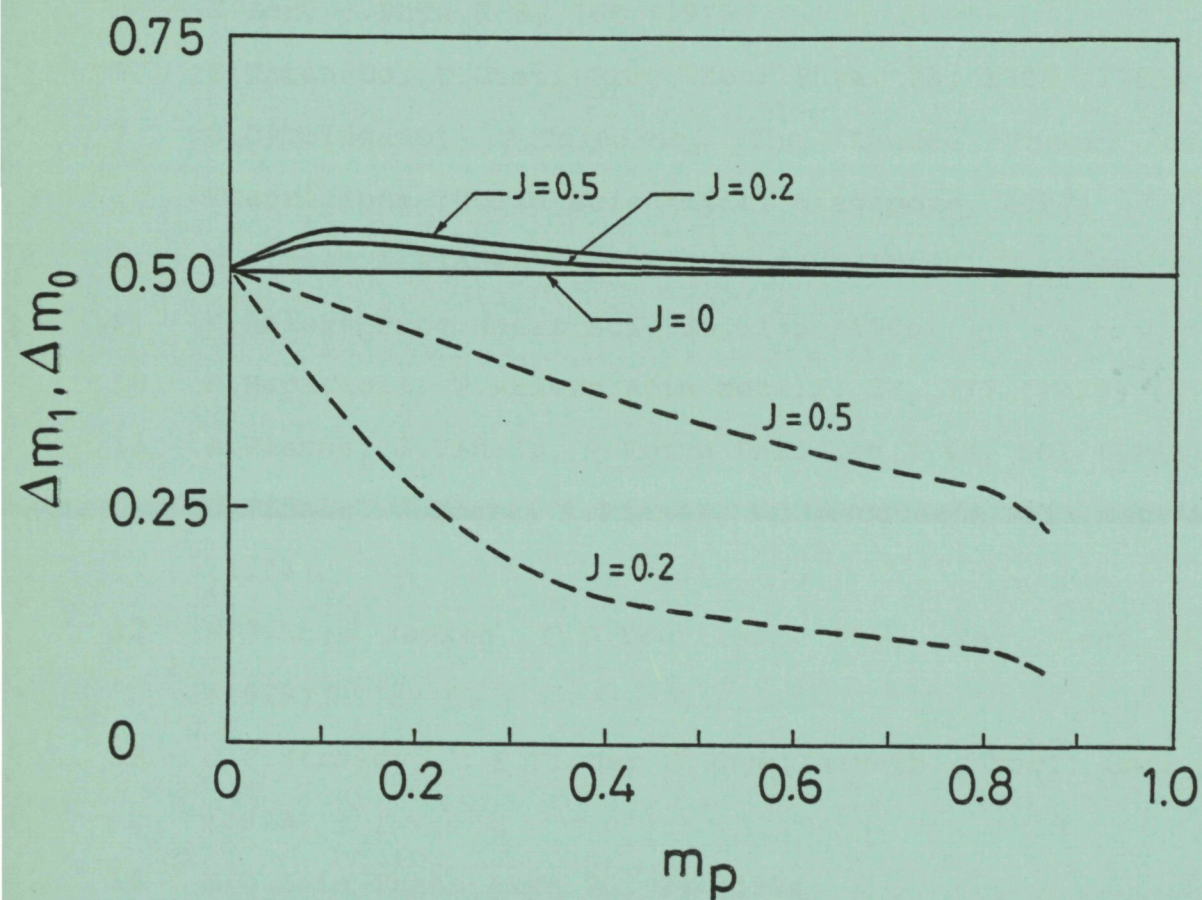22   F. Falk, P. Konopka, J. Phys.:Condens. Matter **2**, 61 (1990).

Fig.1 Discontinuity of the order parameters at the transition point versus m_p in the case J=0.2 and J=0.5. Continuous lines correspond to Δm_1 and dashed lines to Δm_0. The continuous line at $\Delta m = 0.5$ corresponds to the case J = 0 ($\Delta m_1 = \Delta m_0 = \Delta m$).
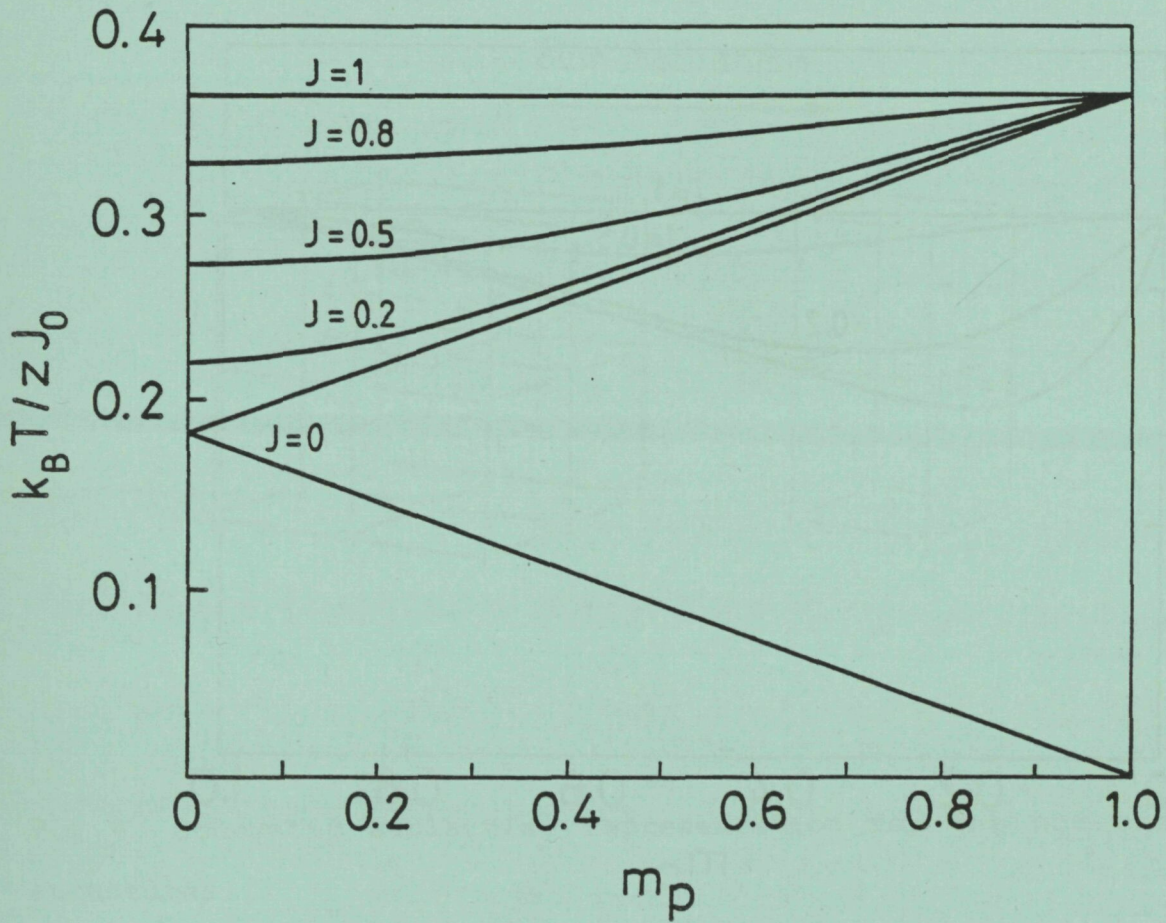
Fig.2 Phase diagram showing the transition temperature lines for J=0, 0.2, 0.5, 0.8 and 1 as a function of the configurational order parameter m_p. Note the splitting off in two phase transition when J = 0, as explained in the text.
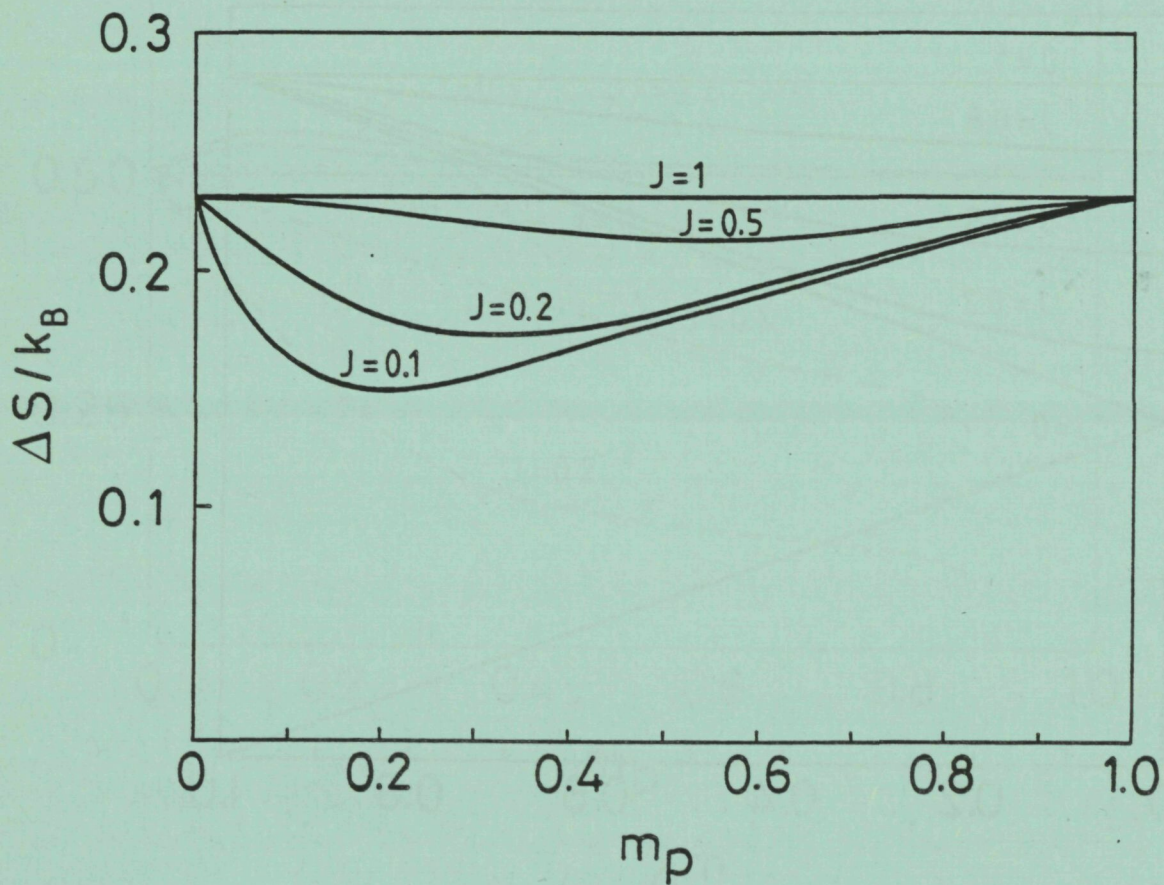
Fig 3. ΔS values for J=0.2, 0.5 and 1 as a function of m_p.