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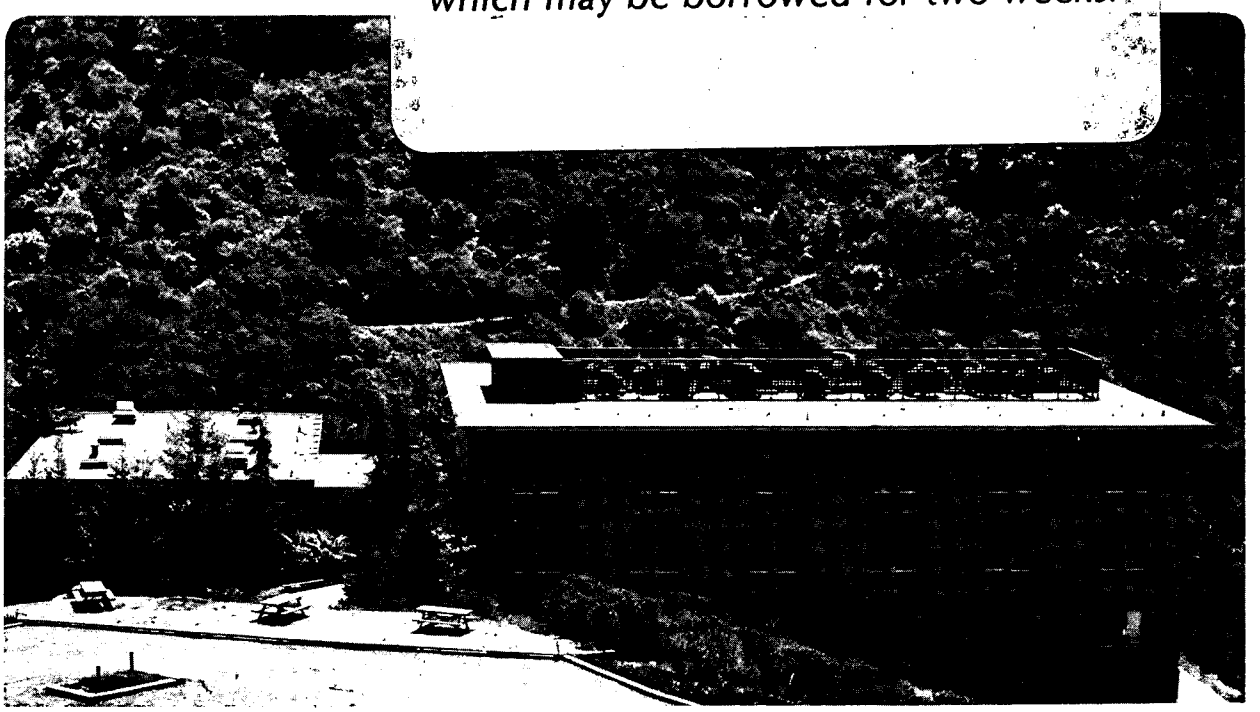

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Abstract. Ordered superstructures consisting of occupied and empty oxygen sites in the $Cu-O$ basal plane of $YBa_2Cu_3O_z$ have been determined. Pairwise interactions (V_1,V_2,V_3) between nearest and next nearest neighbor sites are assumed and ordering maps are plotted as a function of V_2/V_1 and V_3/V_1 (in the ordering case : $V_1 > 0$). The ground state of this Ising model is determined by a direct enumeration method and the relation with experimentally obtained structures is discussed.

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The crystal structure of the high temperature superconductor $YBa_2Cu_3O_z$ ($z = 7-\delta$) has been investigated by X-ray [1-4], neutron [5-9] and electron diffraction and microscopy [10-11]. Both a tetragonal (P4/mmm) and an orthorhombic (Pmmm) phase have been identified : the latter is the superconducting one. It is now well documented that the superconducting properties depend critically on the presence of $Cu-O$ chains parallel to the orthorhombic b axis. Furthermore, the oxygen content must be close to, or somewhat less than the stoichiometric value $z = 7$ ($\delta = 0$). The orthorhombic phase transforms on heating to the tetragonal phase at about 700 C. The transition is marked by a disordering of oxygen ions and structural vacancies on the O sites of the Cu_2O basal plane. Other O sites, outside the basal planes, appear to be largely unaffected by the two-dimensional ordering. Hence we may take the concentration of filled sites in the basal plane to be $c_o = (z-6)/2$. The study of the thermodynamics of this two-dimensional order-disorder transition is clearly crucial to the understanding of the superconducting properties of the compound of interest. The present contribution addresses the ordering ground states in the basal plane.

Ordering instabilities in two-dimensional k-space were investigated in a previous publication [12]. The model shown in Fig. 1 was adopted. Were it not for the presence of Cu atoms this would be a simple square Ising model with cell edges at 45° to the horizontal axis in the figure. The Cu atoms, however, break the symmetry : the centers of alternate square cells are occupied by Cu in checkerboard fashion. There is thus a unique first-neighbor Ising pair interaction V_1, along cell edges, and two types of second-neighbor pair interactions along the diagonals, V_2 and V_3, the first mediated by Cu, the other not. Apart form modifying the strength of the pair interactions, the Cu ions play no further role in the ordering analysis. These effective pair interactions (EPI) V_r may be given an operational definition :

$$V_r = \frac{1}{4}[W_r(O-O) + W_r(\square-\square) - 2W_r(O-\square)] \qquad (1)$$

where O denotes filled and □ empty oxygen sites. Each quantity W_r on the right of the equal sign in Eq. (1) can in turn be defined as the total energy of the designated pair embedded in a medium consisting of a completely random distribution of O and □ sites [13]. It is seen that $V_r > 0$ favors unlike and $V_r < 0$ like pair formation. The EPI are expected to depend on the full three-dimensional nature of the system, that is on the basal plane oxygen concentration c_o as well as on the nature of the other metallic ions in the compound. The particular geometry of the basal plane was handled in our earlier paper by subdividing the structure into three interpenetrating square sublattices : one for the Cu sites, and two for the O sites, the latter two being denoted by the labels α and β (see Fig. 1). The V_1 interaction then couples the α and β sublattices; V_2 and V_3 act on pairs of sites belonging to just one sublattice.

The Hamiltonian for the Ising model with sublattices α, β can be written [12]

$$H = \frac{1}{2} \sum_{m,m'} \sum_{n,n'} v(\mathbf{R}_m + \rho_n - \mathbf{R}_{m'} - \rho_{n'})\, \sigma(\mathbf{R}_m + \rho_n)\, \sigma(\mathbf{R}_{m'} + \rho_{n'}) \qquad (2)$$

where $\mathbf{R}_m$ is a lattice vector and ρ_m is a position inside the unit cell; in the present case $\rho_n = (0,0)$ for sublattice α and $\rho_{n'} = (½,½)$ for sublattice β, for example. The pseudo-spin variables σ denote site occupancy, taking values +1 if a site is occupied by an O ion, -1 if it is empty. The summations run over all sites, taking into account the implicit cut off due to the short range of the interactions. In the present case, the interactions v take the values V_1, V_2, V_3 as defined above (see Fig. 1).

In our previous paper, a stability analysis was conducted by rewriting the Hamiltonian (2) in k-space representation, then expressing H as a sum of amplitude-squared of "normal concentration modes" [14-15]. Ordering instabilities are expected for those k-values for which the associated concentration wave has lowest energy (for unit amplitude). Instabilities are expected at so-called Special Points (SP) in k-space where symmetry elements intersect (Lifshitz criterion). The SP relevant to the present problem are the Brillouin zone center

<00>, and the zone boundary points <½0> and <½½>. Which SP will have, associated with it, the lowest energy wave will depend on the values of the normalized interaction parameters $x = V_2/V_1$ and $y = V_3/V_1$. For $V_1 > 0$ (nearest neighbor ordering), regions were mapped out in x,y space where a given SP wave would lead to an ordering instability [12].

Such a stability analysis gives information about incipient instability; ordering waves modulate the lattice and may give rise to fractional occupation of lattice sites. To insure that actual crystal structures are described, with O or □ occupation at each site, combinations of ordering waves, belonging to different stars, may be required. It is then simpler to perform the analysis in direct space by seeking those combinations of +1 and -1 occupation variables σ which give H in equation (2) its minimum value for given interaction parameter ratios. There result ground state maps which show regions in x,y space where a given ordered superstructure has minimum value for a selected stoichiometry c_o. To derive such maps we have generated all possible configurations on a 2x2 and a 2x4 lattice, containing 8 and 16 oxygen sites respectively. Subsequently we determined which structure minimized the Hamiltonian (1) in the different regions of the xy-plane. In view of the method used we cannot completely rule out the possibility of a ground state that is not compatible with the multiple unit cells that we chose. However, as will become clear from our results such a possibility appears extremely unlikely.

At concentration $c_o = 0.50$, we find the ground state map of Fig. 2. The boundaries of the ground state regions agree exactly with those derived earlier for the stability analysis [12]. Hence we have indicated in each region both the unit cell of the ordered structure and the unstable wave vector. The appropriate two-dimensional space group symbol is also included. In the lower left corner of the figure, <0 0> instability, a simple rectangular structure p2mm is found to be stable. One immediately recognizes the basal plane of the Pmmm orthorhombic structure of the high-T_c superconductor. As explained in the earlier paper, the <00> instability places one type of symbol on one sublattice, say O on α and the

other (□) on β, thus forming the one-dimensional $Cu-O$ chains characteristic of the superconducting phase. The structure p2mg, depicted in the upper right corner can be produced by modulating each sublattice by a <½½> ordering wave. In the other two regions, the stability analysis predicts <½0> instabilities, but only one sublattice becomes modulated by the cell-doubling wave, the other sublattice remaining unmodulated. To produce a definite crystal structure two waves must operate simultaneously : [½0] and [0½], leading to a square quadruple cell with space group p4mm. Except in the top left hand region the Cu-ions have a coordination of 0.50, whereas in the former structure the Cu-ions are either fully coordinated by oxygens or by vacancies.

Figure 3 shows ground state configurations corresponding to an oxygen concentration of $c_o = 0.25$ (or equivalently $c_o = 0.75$). In that case, the stability analysis is no longer directly applicable and one expects to find more complicated structures made up of superpositions of ordering waves. As expected, the stable ground state structures are made up of SP ordering waves belonging to different stars. In the first quadrant ($V_2 > 0$, $V_3 > 0$) of the xy map one sublattice is filled by □ symbols, and the other is modulated by a <½½> wave, producing the quadruple cell c2mm structure shown. Actually, the ground state in that quadrant is infinitely degenerate : the $O-$□ diagonal chains may be translated parallel to themselves with no change in ground state energy since only third-neighbor bonds are altered in the process. In the (+,-) and (-,+) quadrants, p2mm cell doubling structures are produced by a combination of <00> and [½0] or [0½] waves. Finally, the ground state in the (-,-) quadrant can be regarded as produced by a <00> (very long wavelength) ordering wave placing □ symbols on sublattice α and a random mixture of □ and O on β. The β sublattice can then 'phase separate' giving a structure composed of domains of p2mm (ordered) and p4mm (pure vacancy) units.

We believe that the ground state analysis presented here is complete for the range of interactions considered and for $V_1 > 0$. The determination of ordered ground states for a

novel type of Ising model is of intrinsic interest but it is, of course, the application to high-T_c superconductors which motivated the present study. In that regard, the basal plane structures expected are those formed for V_2 and V_3 less than V_1, in magnitude. Thus, the most likely structures to be encountered in practice are (a) the disordered (simple-cell) structure p4mm, corresponding to the three-dimensional tetragonal phase P4/mmm, (b) the simple-cell p2mm structure, close to c_o = ½ stoichiometry (z = 7), corresponding to the orthorhombic phase Pmmm, and, possibly, (c) one of the double-cell p2mm structures at stoichiometry c_o = ¼ (z = 6.5) or c_o = ¾ (z = 7.5).

Evidence for the cell-doubling structure has been obtained by electron microscopy and diffraction, although the observed ½0 diffraction spots are rather weak and diffuse [10-12]. No independent X-ray or neutron evidence for ½0 diffuse intensity is available, as far as we know. The existence of such a structure at equilibrium is quite plausible, however, since both simple-cell p2mm (three-dimensional orthorhombic structure) and double cell p2mm are mutually compatible. If the effective pair interactions are concentration independent (which is by no means certain) it suffices to take, for the range of V's, the overlap of appropriate regions in the c_o = ½ and c_o = ¼ maps, i.e. $V_1 > 0$, $V_2 < 0$ and $0 < V_3 < V_1$.

Given presently available structural information on $YBa_2Cu_3O_z$ or similar compounds, the following scenario appears to be a likely one : the stable low temperature phase at or near z = 7 is the orthorhombic Pmmm with basal plane ground state p2mm (simple near-square cell), consisting of one filled, one empty sublattice, generated by out-of-phase <00> ordering waves [12]. If the sample were to be heated at constant oxygen content, it would eventually transform to the tetragonal phase (simple cell, p4mm). Actually, at constant oxygen partial pressure, oxygen loss occurs progressively on heating [9], so that, by the time the disordering temperature is reached, the system will be far from c_o = ½ stoichiometry, which may promote the p2mm cell-doubling phase. For that phase, or for the simple-cell phase off stoichiometry, the disordering temperature is expected to be lower than that at stoichiometry.

That is because only at $c_o = ½$ are the near neighbor pair relations, required by the signs of V_1, V_2, V_3, strictly satisfied. The fact that very weak extra ordering spots were detected could mean that, at these high cooling rates required to retain the low oxygen content, the ordering kinetics are too slow to reach full equilibrium.

Note finally that the only basal plane structure that contains infinite [010] $Cu-O$ chains is the p2mm <00> structure close to stoichiometry. At c_o close to 1/4 the <00> instability gives rise only to isolated chain structure domains. Since these chains appear to be essential for high-T_c superconductivity, transitions to either the disordered p4mm or ordered cell doubling p2mm severely reduce the superconducting transition temperature.

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References.

[1] T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava and S. M. Zahurak, Phys. Rev. B **35**, 7137 (1987).

[2] J. van den Berg, C. J. van der Beek, P. H. Kes, G. J. Nieuwenhuys, J. A. Mydosh, H. W. Zandbergen, F. P. F. van Berkel, R. Steens and D. J. W. IJdo, preprint submitted to Europhys. Lett.

[3] M. P. A. Vliegers, D. M. de Leeuw, C. A. H. A. Mutsaers, H. C. A. Smoorenburg, J. H. T. Hengst, J. W. C. de Vries and P. C. Zalm, preprint.

[4] J. J. Caponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence and R. Tournier, Europhysics Lett. **3**, 1301 (1987).

[5] M. A. Beno, L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, I. K. Schuller, C. U. Segre, K. Zhang and J. D. Grace, Appl. Phys. Lett. **51**, 57 (1987).

[6] F. Beech, S. Miraglia, A. Santoro and R. S. Roth, Phys. Rev. B (in press).

[7] C. C. Torardi, E. M. McCarron, M. A. Subramanian, H. S. Horowitz, J. B. Michel, A. W. Sleight and D. E. Cox, preprint.

[8] J. D. Jorgensen, B. W. Veal, W. K. Kwok, G. W. Crabtree, A. Umezawa, L. J. Nowicki and A. P. Paulikas, preprint submitted to Appl. Phys. Lett.

[9] J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang and M. S. Kleefisch, preprint submitted to Phys. Rev. B.

[10] G. Van Tendeloo, H. W. Zandbergen and S. Amelinckx, preprint submitted to Sol. St.

Comm.

[11] H. W. Zandbergen, G. Van Tendeloo, T. Okabe and S. Amelinckx, preprint submitted to phys. stat. sol. (a).

[12] D. de Fontaine, L. T. Wille and S. C. Moss, Phys. Rev. B (in press).

[13] D. de Fontaine in "Lecture Notes of International School on Electronic Band structure and its Applications.", (M. Yussouf, ed.) Springer Verlag (1987).

[14] J. M. Sanchez, D. Gratias and D. de Fontaine, Acta Cryst. **A38**, 214 (1982).

[15] A. G. Khachaturyan and G. A. Shalatov, Acta Metall. **23**, 1089 (1975).

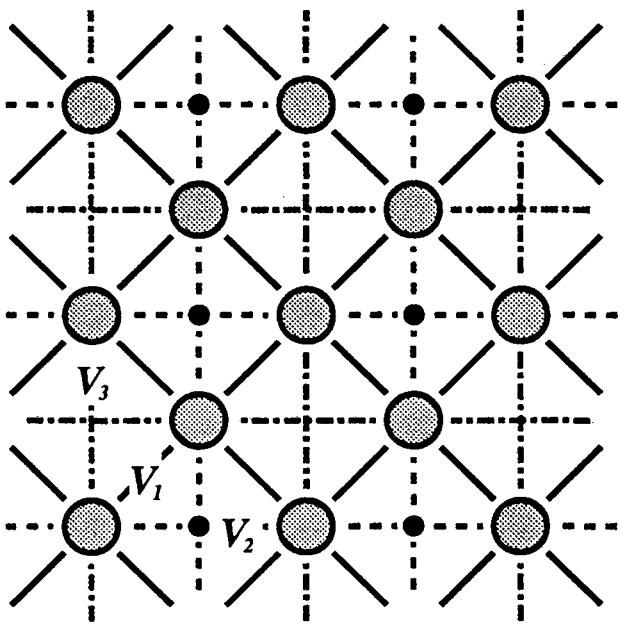
Figure Captions.

1. Sublattices in the basal plane of $YBa_2Cu_3O_z$ structure. Black dots : Cu atoms, open circles O sites. Effective pair interaction V_1 couples the two oxygen sublattices α and β; V_2 and V_3 operate on one sublattice.

2. Ground state map ($V_1 > 0$) at $c_o = 0.50$. Two-dimensional space group symbols are indicated along with corresponding special point wave.

3. Ground state map ($V_1 > 0$) at $c_o = 0.25$. Note that the structure in the upper right quadrant is infinitely degenerate (see text).

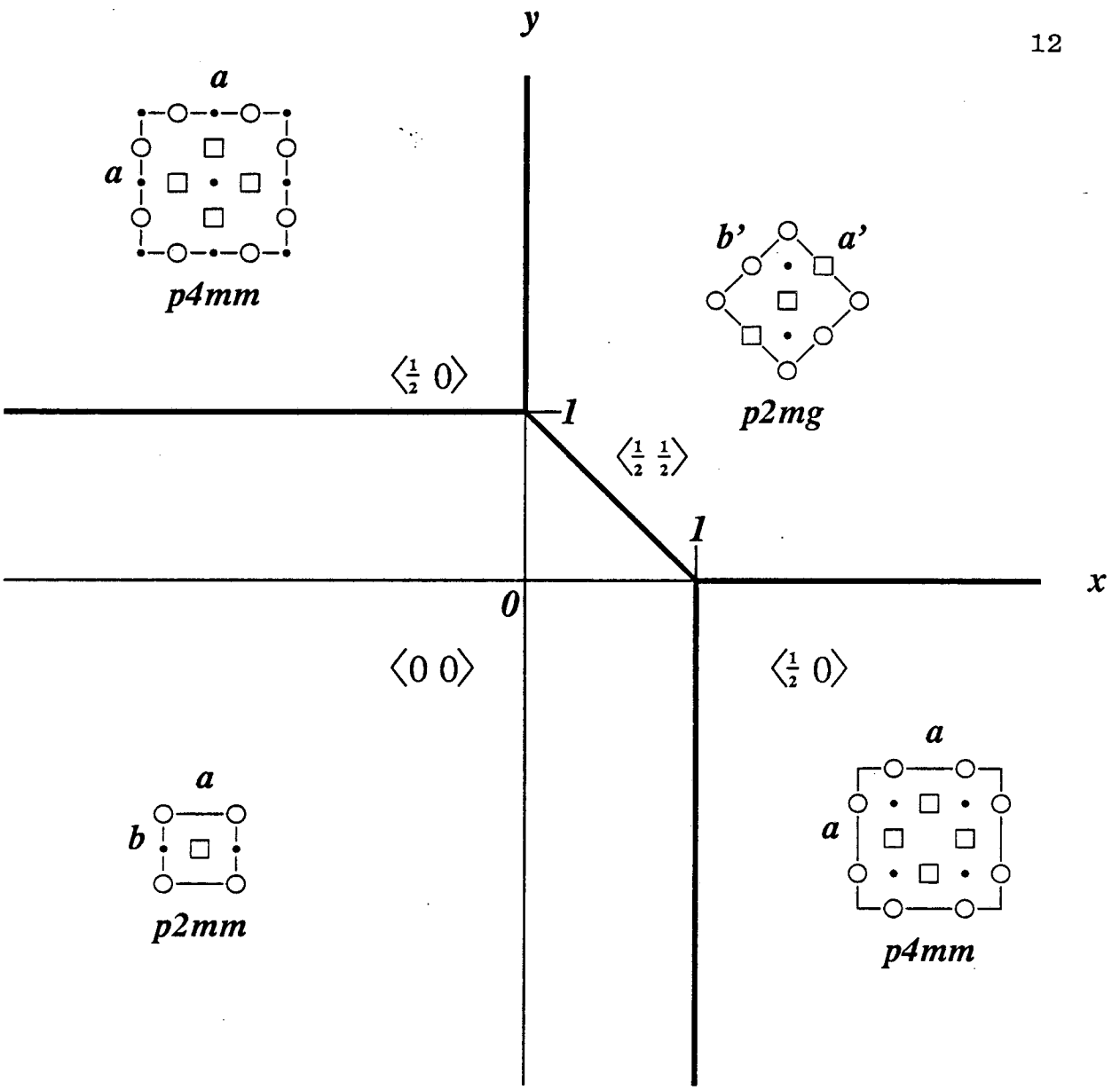
Figure 1



Disorder

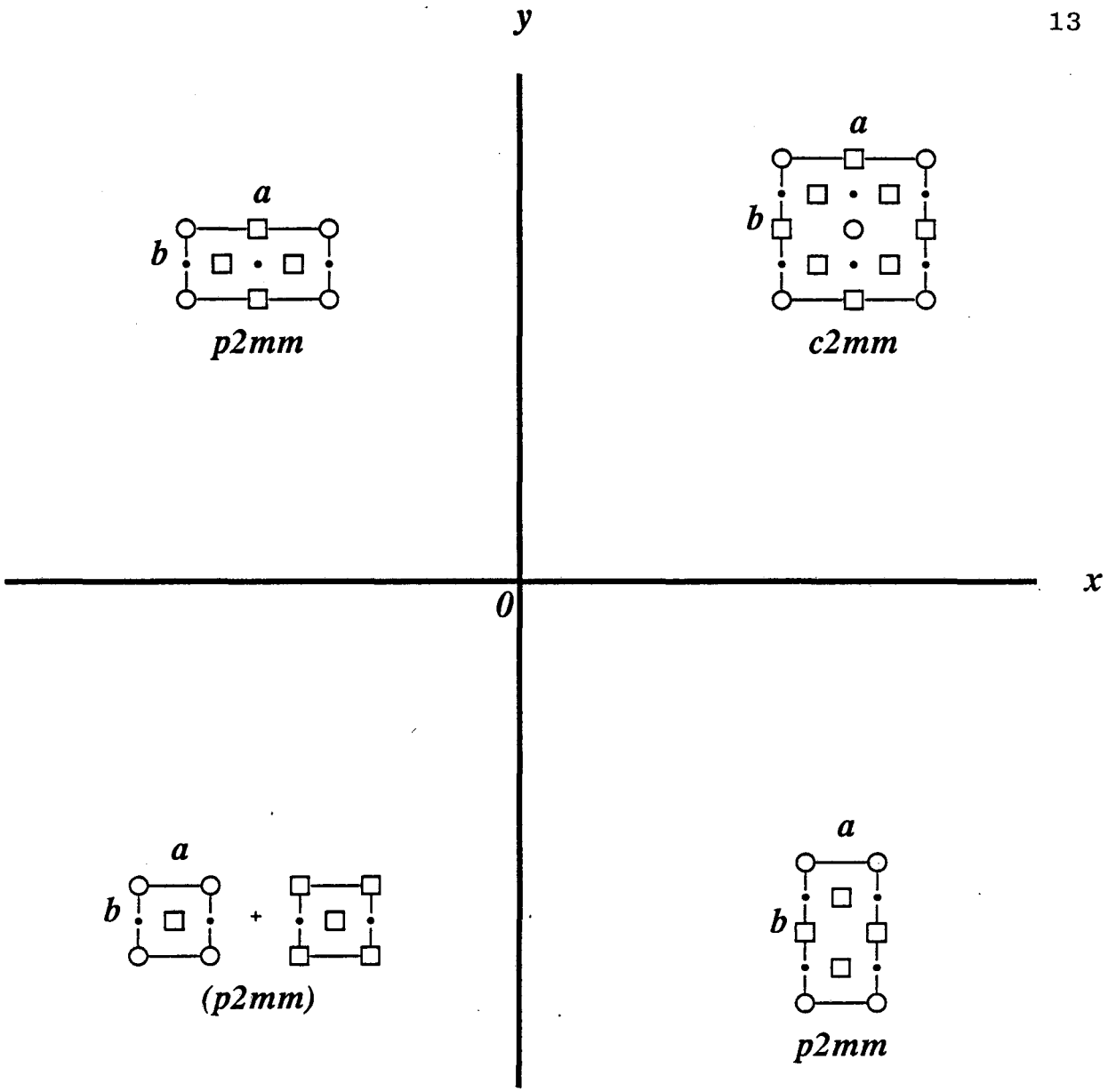
p4mm

$a=b=a_0$



$V_1 > 0,\ c_0 = 1/2$

Figure 2



$V_1 > 0,\ c_0 = 1/4$

Figure 3

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